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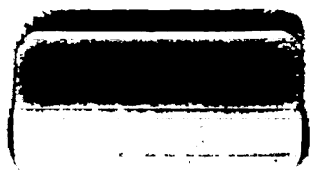
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AN INTRODUCTION TO THE STUDY OF ORGANIC CHEMISTRY,

BY

H. T. CLARKE

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Essent. Principles of org. chem
James Conon



WITH DIAGRAMS

LONGMANS, GREEN, AND CO.

39 PATERNOSTER ROW, LONDON

FOURTH AVENUE & 30TH STREET, NEW YORK

BOMBAY, CALCUTTA, AND MADRAS

1914

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PREFACE

IN the writing of text-books of Organic Chemistry there are two distinct and incompatible systems. In the one, it is the practical aspect of the science which is kept in chief view; in the other, its symmetry and homogeneity. The one constantly directs attention to detail; the other approaches the subject with the desire of displaying its orderly principles and structural unity. The present writer adheres with conviction to the latter method.

The reader of text-books based upon the practical point of view is apt, if he be a beginner, to lose the thread of the argument in the wealth of facts; for the mass of information necessary for the proper comprehension of the main principles of organic chemistry is so great, that additional details hinder rather than assist the student in his laborious task of assimilation.

Even more important is the following consideration. Of recent years there has been an increasing tendency in examinations to set questions intended to be answered "with all essential practical details"—a procedure designed to test the practical training of candidates. No real knowledge of organic chemistry can be acquired without laboratory work; and to supply in a small text-book, covering the entire field, these practical details, so that they can be memorised without actual experience, is contrary to the best interests of students.

The present volume has been written to meet the new syllabus (1912) of the lower examination in organic chemistry in the Board of Education Examinations in Science and Technology. Previous knowledge of inorganic chemistry, though not of organic chemistry, is assumed. It is hoped that the matter here presented may also meet the needs of candidates for the Medical examinations in organic chemistry; with this in view, some of the more advanced portions, not intended for the Medical curricula, have been printed in smaller type.

The customary order of presentation—in which the methods of purification and analysis are discussed at the outset—has been modified. Since the reader is assumed to be entirely unfamiliar with the nature of organic substances, it would be illogical to begin with a discussion of the methods by means of which their formulæ have been determined; for this reason the first two chapters are devoted respectively to an exposition of the simplest features of the chemistry of carbon compounds and to the relations of the more important derivatives obtainable from ethyl alcohol. In the second chapter the ground is traversed with extreme rapidity, the aim being merely to allow the student to familiarise himself with the structural formulæ of the chief types of aliphatic compounds before proceeding to a discussion of the methods of elementary analysis. This chapter, in particular, should pave the way for the subsequent description of the properties of the different classes of organic compounds.

In preparing this volume, free use has been made of the more important text-books of organic chemistry; the writer desires, more particularly, to acknowledge his indebtedness to Meyer and Jacobson's *Lehrbuch der Organischen Chemie*.

In conclusion, it is the writer's agreeable duty to express his thanks to Dr. A. W. Stewart, Dr. Samuel Smiles, and Mr. J. I. O. Masson for valuable suggestions, and especially to Dr. Stewart for reading the proofs and for his permission to reproduce certain diagrams from his treatise on "Stereochemistry."

H. T. CLARKE.

University College, London,
March, 1914.

CONTENTS

CHAPTER	PAGE
I. INTRODUCTORY	I
II. CLASSES OF COMPOUNDS DERIVED FROM ETHYL ALCOHOL .	29
III. METHODS OF PURIFICATION AND ANALYSIS	49
IV. DETERMINATION OF MOLECULAR WEIGHT	63
V. HYDROCARBONS	73
VI. HALOGEN COMPOUNDS	91
VII. ALCOHOLS	106
VIII. ETHERS	135
IX. ALDEHYDES AND KETONES	140
X. SIMPLE MONOCARBOXYLIC ACIDS AND THEIR DERIVATIVES .	157
XI. SIMPLE DICARBOXYLIC ACIDS AND THEIR DERIVATIVES .	178
XII. ESTERS OF INORGANIC ACIDS	192
XIII. AMINES	198
XIV. NITROPARAFFINS	206
XV. ORGANIC COMPOUNDS OF SULPHUR	209
XVI. CYANOGEN COMPOUNDS	216
XVII. ALKYL DERIVATIVES OF METALS AND NON-METALS . .	232
XVIII. HYDROXYACIDS	241
XIX. ALDEHYDIC AND KETONIC ACIDS	258
XX. MALEIC AND FUMARIC ACIDS	265
XXI. CARBOHYDRATES	270
XXII. AMINO ACIDS	288
XXIII. URIC ACID AND PURINES	296
XXIV. AROMATIC COMPOUNDS	300
XXV. BENZENE AND ITS HOMOLOGUES	319
XXVI. HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES	326

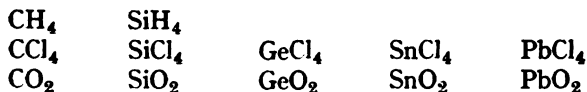
CHAPTER	PAGE
XXVII. AROMATIC DERIVATIVES OF SULPHUR	332
XXVIII. HYDROXY DERIVATIVES OF BENZENE AND TOLUENE .	337
XXIX. AROMATIC NITRO COMPOUNDS	350
XXX. AROMATIC AMINO COMPOUNDS AND THEIR DERIVATIVES	358
XXXI. AROMATIC COMPOUNDS CONTAINING NITROGEN ATOMS DIRECTLY UNITED	373
XXXII. AROMATIC ALDEHYDES AND KETONES	384
XXXIII. AROMATIC CARBOXYLIC ACIDS	391
XXXIV. CONDENSED BENZENOID SYSTEMS	406
XXXV. MECHANISM OF SUBSTITUTION IN AROMATIC COMPOUNDS	422
XXXVI. CHIEF CLASSES OF DYESTUFFS	429
XXXVII. ALICYCLIC AND HETEROCYCLIC COMPOUNDS	449
SUMMARY	460
PROBLEMS	474
INDEX	477

ORGANIC CHEMISTRY

CHAPTER I

INTRODUCTORY

THE element Carbon stands at the head of the fourth column in the Periodic Table. The characteristic property of the members of this series is their power to form compounds with either four atoms of hydrogen, four atoms of halogen, or two atoms of oxygen :



At the beginning of the last century, compounds of carbon were known to chemists, but, with the exception of carbonic acid and metallic carbonates, these were all products of organic—that is to say, of animal or vegetable—life. Examples of such substances are: fats and gelatine, from animal life; sugar, alcohol, vinegar, and starch, from vegetable life. None of these products of living organisms had at that time been synthesised in the laboratory; they were hence regarded as having been produced by a *vital force* in organic life, which was not, and never could be, under the control of the chemist. These substances—some of which had been accurately investigated—were therefore called Organic compounds, and their study came to be known as Organic Chemistry. A further difference, at first regarded as fundamental, was found in the

fact that, unlike most inorganic compounds, these organic bodies were destroyed on heating to a high temperature.

But at the beginning of the second quarter of the nineteenth century chemists began to find out that these very compounds of carbon could be transformed into and out of simpler substances, and could even be built up from their elements. The original significance of the term "organic" thus fell away on its being recognised that there is no difference between the chemistry of carbon compounds and that of any other compounds; the name has nevertheless been preserved for convenience of designation, since organic chemistry has peculiar processes and ideas so numerous and so pronounced as to demand separate study.

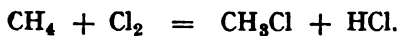
Organic chemistry concerns itself primarily with bodies derived from carbon tetrahydride CH_4 , generally known as **methane**. This substance occurs in nature in the "fire-damp" in many coal-mines, and also forms a large proportion of the gas which is evolved from the decaying vegetable matter in marshes and stagnant pools. Hence a frequent name for it is "marsh gas." It is the simplest member of a large class of compounds, containing only carbon and hydrogen, known as **hydrocarbons**.

Now it has been found that when methane is treated with chlorine in diffused daylight, a mixture is obtained of products which contain carbon, hydrogen, and chlorine, together with one which contains only carbon and chlorine. On separating these substances by fractional distillation and analysing them, we find that the composition of the various pure constituents may be expressed by the formulæ :

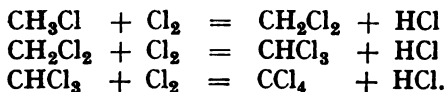


Moreover, we find that the reaction-mixture contains gaseous hydrogen chloride, as well as some unchanged methane.

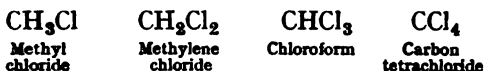
From this we are able to deduce that the chlorine withdraws hydrogen from the methane, combines with it to form hydrogen chloride, and at the same time replaces the hydrogen atom it so removes. The reaction may be expressed thus :



If we treat a pure sample of this carbon trihydride-monochloride again with chlorine, we find in the reaction-mixture the same four substances CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 , together with hydrogen chloride. This confirms our hypothesis of the replacement of hydrogen by chlorine, indicating that the reaction may be subdivided into three stages, viz. :



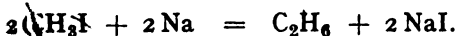
These compounds are named as follows :



The radicle $-\text{CH}_3$ is termed *methyl*, the radicle $-\text{CH}_2-$ is termed *methylene*. Similar compounds of bromine and iodine exist, such as for instance *methyl bromide* CH_3Br , and *methylene iodide* CH_2I_2 .

Now if we treat a methyl halide, such as methyl iodide, with metallic sodium, the halogen atom is removed, with production of sodium halide. But in this case a metallic atom does not replace the halogen ; we obtain instead a gas of which the analysis corresponds with the composition CH_3 . At first sight we might be led to the conclusion that the valency of the carbon atom has been reduced from four to three, and that carbon trihydride has been produced. That this is not the case is shown by a determination of the density of the gas (see p. 64), which is found to be double that required for the formula CH_3 . This new gas must therefore have the composition C_2H_6 .

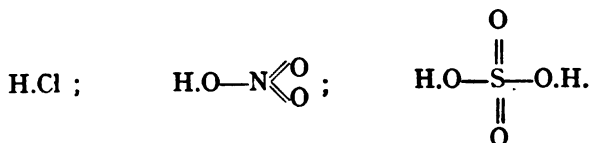
We may formulate the reaction thus :



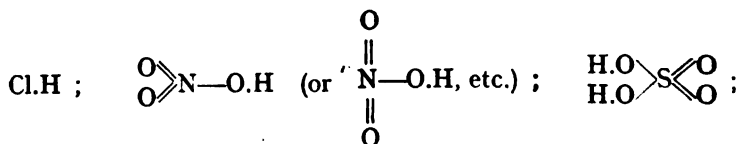
Now if we conclude that hydrogen remains in all cases univalent, the only conclusion we can draw is that the carbon atoms are directly united, $\text{H}_3\text{C}-\text{CH}_3$. This new gas, known as **ethane**, resembles methane in many of its properties, being similarly

sluggish in its reactions, but it possesses a higher boiling-point and differs likewise in other physical properties.

In inorganic chemistry we make a practice of assigning, whenever possible, some definite structure to the formula designating a compound, in which we depict definite atoms as being attached to other atoms by "bonds" representing the valencies exerted by the various atoms. Examples of these are hydrochloric acid, nitric acid, and sulphuric acid :



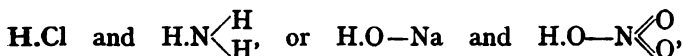
The precise manner in which these formulæ are written is of course immaterial, so long as the disposition of the strokes or dots indicating the bonds remains essentially the same. We may equally well write the formulæ thus :



or in any other convenient manner.

This system serves as a sort of shorthand method of explaining how we regard the atoms in a molecule to be related to one another, basing our formulæ on considerations of the chemical properties of the substance in question. To a great extent we really believe that the atoms are actually situated in such a manner with respect to one another ; but first, as gas some such a structural formula is merely our mode of expressing the reactions of a compound. In addition to the many other advantages to be derived from a graphic formula, we are enabled to make clear our conception of the distribution of the valencies. It must, however, be borne in mind that any shorthand system always carries with it certain

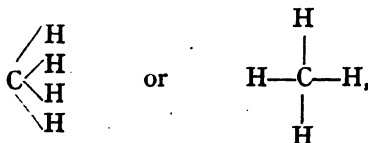
tacit assumptions which we must read into the interpretation. We must, for instance, realise the different chemical attributes of a hydrogen atom or a hydroxyl group when in varying situations. In the formulæ :



the chemist attaches totally different conceptions of chemical activity to the hydrogen atoms and hydroxyl groups in their different surroundings.

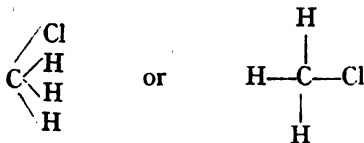
Similarly, in organic chemistry, it is absolutely necessary to employ graphic formulæ. The reasons for this will shortly become apparent.

Methane is shown, by analysis and from a consideration of its physical properties, to consist of molecules containing one carbon atom and four hydrogen atoms. As the valency of hydrogen is taken as unity, we have no alternative but to express the constitution of methane by some such ideograph as :



a formulation which clearly expresses the quadrivalency of the carbon atom.

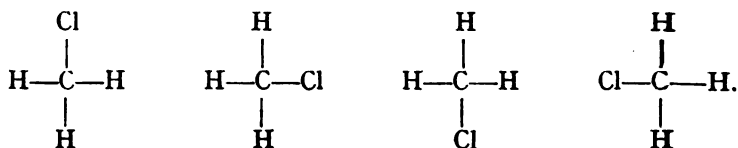
On allowing chlorine to react with methane we obtain monochloro-methane, usually termed methyl chloride, CH_3Cl . A chlorine in most of its compounds behaves as a univalent element, there is no reason why we should regard the chlorine in methyl chloride as exerting a higher valency. We therefore formulate methyl chloride thus :



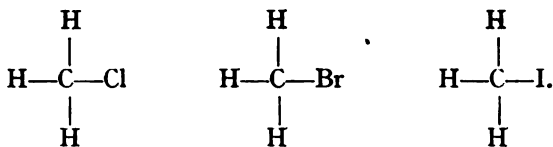
By this formulation we assume the valency of the carbon atom to be four; and throughout organic chemistry the guiding assumption in the formulation of compounds of carbon is the constancy of the quadrivalency of that element. It has been due almost entirely to the adherence to this fundamental principle that systematic organic chemistry owes its existence.

One, and only one, compound of the empirical formula CH_3Cl is known. From this fact we draw the conclusion that all the four hydrogen atoms in methane stand upon the same footing—that it is immaterial which of the four is replaced by the chlorine atom. They are said to be *equivalent*.

In reading the meaning into the formula for methyl chloride we must therefore realise that precisely the same significance is to be attached to the four ideographs :

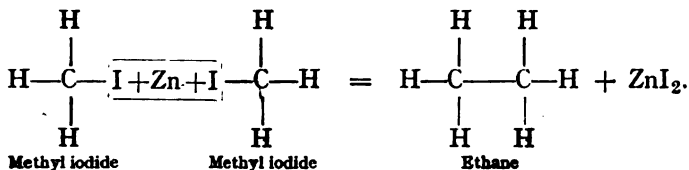


The other methyl halides may be formulated in the same way :



In each of these latter cases there exists but one substance corresponding with each formula.

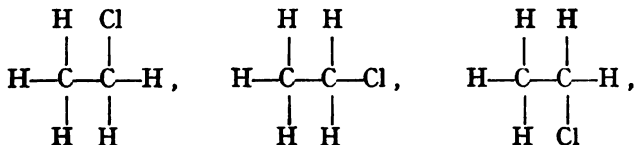
When we treat methyl iodide (the chloride and bromide are gases, and consequently less convenient to handle experimentally) with a metal such as sodium or zinc, we obtain a compound the empirical formula of which is C_2H_6 . To this we have no alternative but to assign the following constitutional or graphic formula :

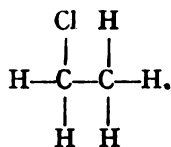
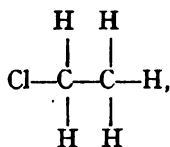
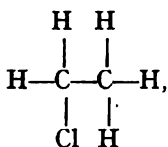


Here the carbon atoms are depicted as being directly united ; and, as we shall see later, the chemical behaviour of ethane is in entire harmony with this conception. This compound, which is the only known substance possessing the molecular formula C_2H_6 , may be regarded as "dimethyl" or "mono-methyl-methane." These terms are self-explanatory, clearly defining the ideas they are intended to convey. The same statement holds good for the synonymous terms "methyl chloride" and "mono-chloro-methane," the different names describing the same compound from different points of view.

When ethane is allowed to interact with chlorine in diffused daylight, we again obtain a mixture of hydrogen chloride and compounds containing carbon, hydrogen, and chlorine, of which we may consider in particular the monochlorinated product $\text{C}_2\text{H}_5\text{Cl}$. This compound, *ethyl chloride*, can be prepared in a variety of ways, but from whatever source they be obtained, substances found by analysis to possess the formula $\text{C}_2\text{H}_5\text{Cl}$ have invariably identical chemical and physical properties.

Ethyl chloride (the name *ethyl* is applied to the radicle C_2H_5 —, which can combine with other radicles or atoms, like the radicle *methyl*), may be regarded from different points of view, as "methyl-methyl chloride," "mono-chloro-ethane," or simply "ethyl chloride," but is, like methyl chloride, a chemical individual. In other words, all the hydrogen atoms are equivalent, as in methane ; and it makes no difference which of the six hydrogen atoms is replaced by the chlorine atom. The following formulæ all represent one and the same compound—ethyl chloride :

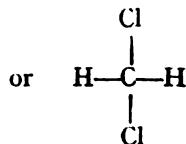
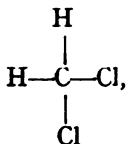
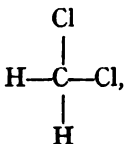
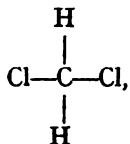




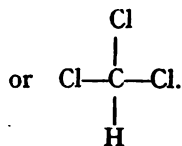
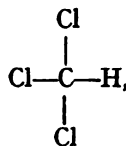
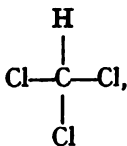
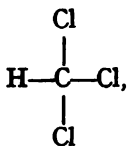
There is no cryptic virtue in this arrangement of writing the valencies at right angles to each other—any other system would serve equally well. This method is merely the most symmetrical and hence the most convenient.

It may here be remarked that substances CH_3 and C_2H_5 , corresponding to "methyl" and "ethyl" are unknown, and are presumed to be incapable of independent existence.

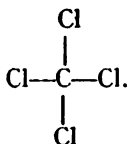
In the same way as above, we may write the structures for dichloro-methane (*methylene chloride*) and trichloro-methane (*chloroform*) in several different ways, to all of which we attach exactly the same significance. Thus dichloro-methane CH_2Cl_2 may be written in any of the following ways :



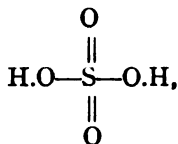
whilst trichloro-methane CHCl_3 may be written as :



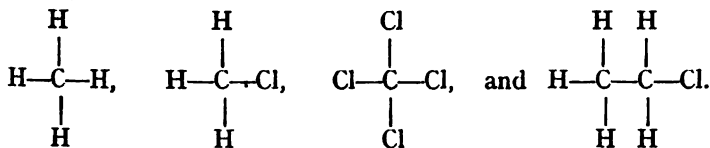
Tetrachloro-methane (*carbon tetrachloride*) CCl_4 , can, like methane, be written in only one way :



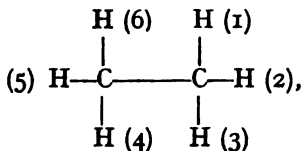
Isomerism.—Up to the present we have discussed organic compounds which may be identified by their empirical formulæ alone : just as by writing the formula H_2SO_4 we at once think of the structure :



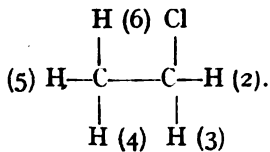
so by writing CH_4 , CH_3Cl , CCl_4 , $\text{C}_2\text{H}_5\text{Cl}$, we are understood to refer to the compounds to which we assign the respective structures :



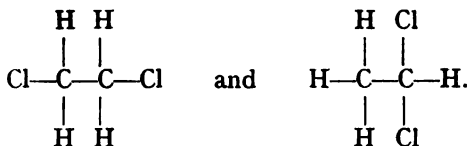
Now when we consider the various ways in which dichloroethane can be written, we are faced with the alternatives : either both chlorine atoms are attached to the *same* carbon atom, or they are attached to *different* carbon atoms. If we label each hydrogen atom in the ethane molecule in the following manner :



we may, on replacing one of these atoms by a chlorine atom, place it indifferently in any of the positions (1) to (6). Let us assume that we replace hydrogen atom (1) by chlorine. We then have monochloroethane or ethyl chloride :



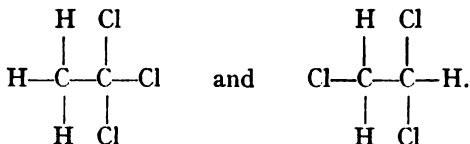
In passing to dichloroethane we can replace any of the hydrogen atoms (2) to (6). The possibilities at once divide themselves into two classes: either we can replace (2) or (3) by a chlorine atom, in which case both chlorine atoms are attached to the same carbon atom, or we can replace (4), (5), or (6) by a chlorine atom, when the resulting compound will contain one chlorine atom attached to each carbon atom. The difference in constitution of the two structures is shown by the two formulæ:



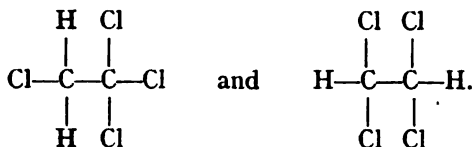
We thus see that it is possible to derive, from purely structural considerations, two distinct formulations for a substance of the empirical composition $\text{C}_2\text{H}_4\text{Cl}_2$. As a matter of fact, there are two compounds known, both of which possess the composition expressed by $\text{C}_2\text{H}_4\text{Cl}_2$, and which are entirely different in chemical and physical properties. It has been established beyond question which of these substances corresponds with each formula, but discussion of this will be reserved for a later chapter (p. 103).

Here we have an example of a phenomenon which occurs but rarely in inorganic chemistry—the existence of two distinct substances, possessing totally different properties, of which the composition and molecular weight are identical. This phenomenon is termed **isomerism** (ἴσος, similar, μέρος, part). Compounds which can be classed under this heading are termed **isomers** or **isomerides**.

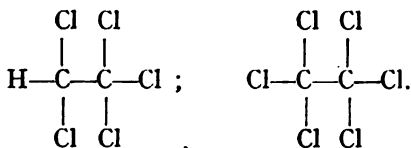
On introducing further chlorine atoms into the ethane molecule, we find that two *trichloroethanes* exist; to these we assign the formulæ:



Similarly there exist two *tetrachloroethanes* :

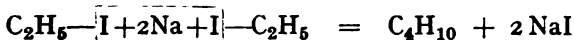


Only one *pentachloroethane* and one *hexachloroethane* are known :

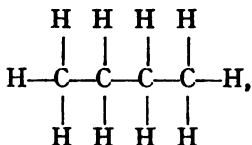


A moment's thought will render clear the reasons why isomerism should exist in some cases and not in others.

Homology.—If a monohalogenated derivative of ethane, such as ethyl iodide, be caused to react with metallic sodium, a reaction similar to that described in the case of methyl iodide takes place :



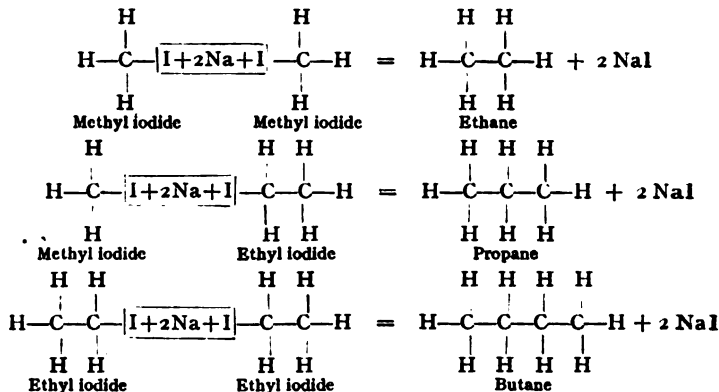
This product C_4H_{10} bears a relation to ethane similar to that of ethane to methane. It is known as **butane**, and must possess the structure expressed by the formula :



since, as we have seen, the carbon atoms to which the halogen atoms were attached are, by this reaction, directly united.

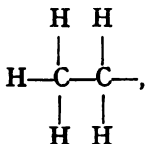
On treating the mixture of ethyl iodide and methyl iodide with sodium, we obtain a mixture of three different hydrocarbons:—ethane, butane, and a new one, **propane**. The sodium may be regarded as exhibiting no particular preference

for the iodine in any individual iodo-compound, so that the following reactions take place simultaneously :

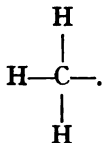


The three products may be separated by fractional distillation.

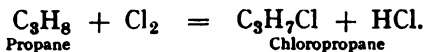
Propane possesses properties which lie intermediate between those of ethane and butane. It may be regarded, from its mode of formation, either as methane, in which one hydrogen atom is replaced by an ethyl radicle :



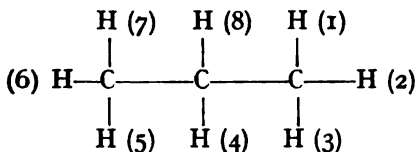
or as ethane, in which one hydrogen atom is replaced by a methyl group :



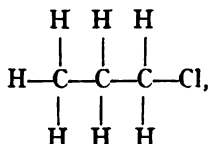
In causing chlorine to interact with propane, we obtain as the first product a *monochloropropane* :



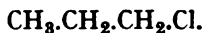
There are in the propane molecule eight hydrogen atoms, any of which may be replaced by a chlorine atom :



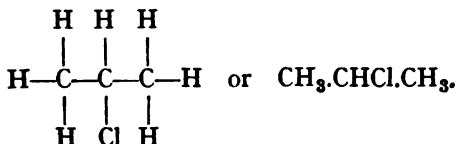
Now, if one of the hydrogen atoms (1), (2), or (3) be replaced, it will be seen that the same chloropropane results in each case. Furthermore, the product will be identical with that produced by substituting one of the hydrogen atoms (5), (6), or (7) ; for a reversal of the pictured structure implies no difference in constitution. In all these cases the chlorine atom is attached to one of the *terminal* carbon atoms, which is itself attached to only *one* carbon atom, and we may write the formula of the product thus :



or, more conveniently,



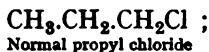
If, on the other hand, we replace either of the atoms (4) or (8) (again it is a matter of indifference which of these two we replace), the chlorine atom will be attached to the *central* carbon atom, which is attached to *two* carbon atoms. The product will then have the structure expressed by :



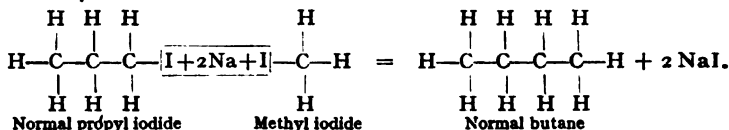
It will be seen that this second chloropropane is different from the first. This structural difference is again borne out by

observation. Two compounds—*isomers*—possessing the same empirical formula C_3H_7Cl , but different properties, have been isolated from the products of the interaction of propane and chlorine. As before, each of these two substances has been identified with the appropriate structural formula by indirect reasoning processes.

The name *normal propyl* (or simply *propyl*) is associated with the first form ; the name *isopropyl* with the second :

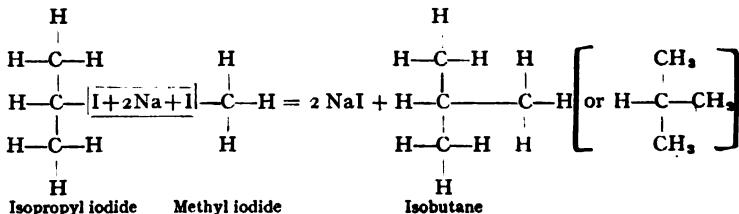


As above stated, on treating ethyl iodide with sodium, we obtain the hydrocarbon C_4H_{10} termed *normal butane* ; the same compound results by the action of sodium upon a mixture of normal propyl iodide and methyl iodide :



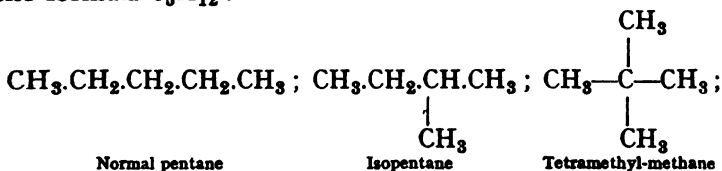
We may thus regard butane as being propane in which a hydrogen atom attached to a terminal carbon atom is replaced by a methyl group.

Now if we allow a mixture of isopropyl iodide and methyl iodide to interact with sodium, we obtain a second compound C_4H_{10} , which possesses properties quite distinct from those of normal butane. This substance must be regarded as propane in which a hydrogen atom attached to the central carbon atom is replaced by a methyl group :



This substance is termed *isobutane* or *trimethyl-methane*. Here we have a case of isomerism in the hydrocarbons.

A great variety of such carbon chains, straight, as in butane, and branched, as in isobutane, can thus be built up by this method. And as the number of carbon atoms in the molecule increases, so does the number of possible isomers increase. Thus there are three compounds corresponding with the formula C_5H_{12} :



five isomeric compounds C_6H_{14} , and so on, until with $C_{12}H_{26}$ there are no less than 355 possible isomers. It will thus be seen what an important part isomerism plays in organic chemistry.

For this reason the student is advised to give little attention to the empirical formulæ of the compound which he is considering ; by correlating the properties of the substances and the structural formulæ assigned to them he will experience no difficulty in grasping the method of this shorthand system, and having once grasped it, the formulation of compounds will resolve itself into a question of reasoning rather than of memory.

The characteristic faculty possessed by carbon atoms, namely that of uniting with each other to form complex "straight-chained" or "branched" systems, is the factor which has caused the distinctive evolution of organic chemistry as contrasted with inorganic chemistry.

Examination of the formulæ of the hydrocarbons CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} , C_6H_{14} , etc., will reveal the fact that their compositions are all expressible by the general formula C_nH_{2n+2} , where n is any number from unity upwards. Each member of the series differs from its predecessor by the increment CH_2 .

The same rule holds good for the mono-halogenated derivatives : CH_3Cl , C_2H_5Cl , C_3H_7Cl , C_4H_9Cl , etc., this series being expressible by the general formula $C_nH_{2n+1}X$, where X

represents Cl, Br, or I. In a series which may be indicated by such general formulæ, the members are termed **homologues**. Thus ethyl iodide and propyl iodide, the formulæ for which differ by a methylene (CH_2) group, are homologues.

In general we may regard the alkyl radicles—or hypothetical residues capable of combining with a hydrogen atom, a halogen atom, and so forth—as forming a homologous series expressible by the general formula $\text{C}_n\text{H}_{2n+1}$:



Unsaturated Compounds.—It is possible to prepare, by various methods, hydrocarbons of the general formula C_nH_{2n} . This can, for example, be effected by the removal of hydrogen halide from a monohalogenated hydrocarbon containing more than one carbon atom. Thus ethyl bromide is converted into a hydrocarbon C_2H_4 by the removal of hydrogen bromide by means of alkali or some similar reagent :

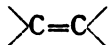


This hydrocarbon is termed **ethylene**. Similarly on removing hydrogen bromide from propyl bromide we obtain the next higher homologue, **propylene**, C_3H_6 :

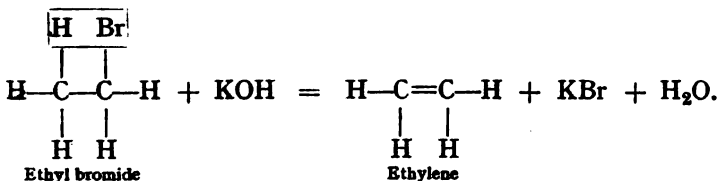


This is a general reaction, and leads to the formation of a series of compounds whose formula may be expressed by C_nH_{2n} .

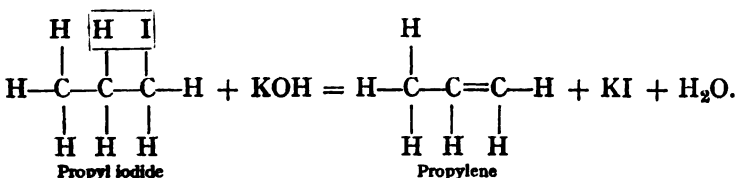
We have no definite proof that in these compounds the valency of two of the carbon atoms has not been reduced from four to three, but the failure to obtain a carbon trihydride is strong presumptive evidence against the correctness of this view. We therefore postulate that carbon remains, throughout the domain of organic—as of inorganic—chemistry, a quadrivalent element. It is thus necessary to assume that two of the valencies of each carbon atom are directly united, and we express this conception by writing a “double-bond” :



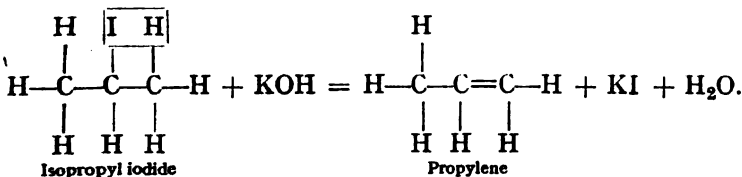
The production of ethylene from ethyl bromide is formulated in the following manner :



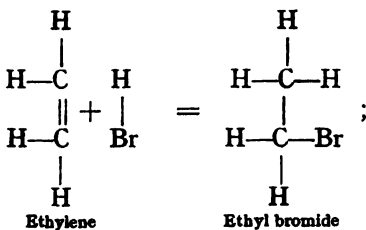
The formation of propylene from propyl iodide follows a similar course :



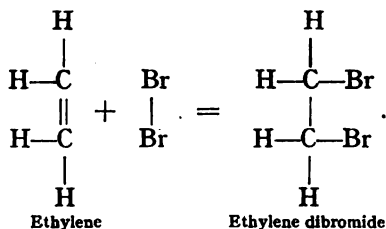
It is to be noted that treatment of isopropyl iodide in this manner yields the same hydrocarbon, propylene :



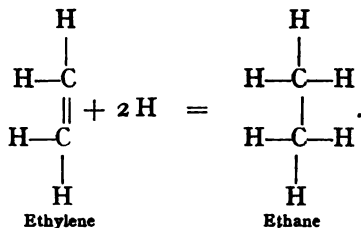
In contrast to the saturated hydrocarbons of the series $\text{C}_n\text{H}_{2n+2}$, the members of this new series C_nH_{2n} , sometimes termed the "olefine" series, are highly reactive. They unite directly with hydrogen halides, with formation of alkyl halides :



and with the halogens themselves, yielding dihalogenated saturated hydrocarbons :

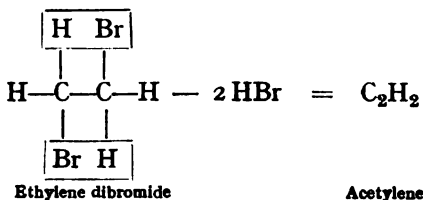


Further, they are readily attacked by oxidising agents (see p. 46) ; and may be reduced, by the action of nascent hydrogen, to the corresponding saturated hydrocarbons, $\text{C}_n\text{H}_{2n+2}$:

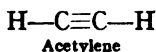


Owing to the readiness with which they unite with halogens and similar reagents, they are known as "unsaturated compounds." The saturated hydrocarbons of the series $\text{C}_n\text{H}_{2n+2}$ are known as "paraffins," owing to their stability towards these reagents (*parum affinis*, of slight affinity).

Now if we eliminate hydrogen halide from the addition-product of a halogen to an olefine, we obtain a second type of unsaturated hydrocarbon, of which the general formula is $\text{C}_n\text{H}_{2n-2}$. Thus ethylene dibromide on treatment with alkali yields a substance C_2H_2 , known as **acetylene** :

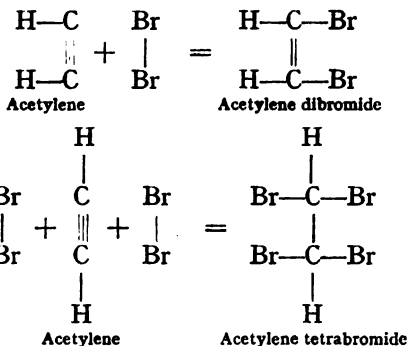


Here again we express our belief in the unaltered quadrivalency of carbon by writing a "triple bond":



The members of the series $\text{C}_n\text{H}_{2n-2}$ are known by the general name of *acetylenes*, and we refer to the two types of unsaturation as *ethylenic* (or *olefinic*) and *acetylenic*.

Acetylenic compounds take up either one or two molecules of halogen, according to the amount presented to them:

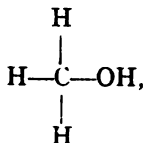


In both series of unsaturated hydrocarbons, homology is possible, resulting in hydrocarbons of the general formulæ C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$ respectively. As in the saturated hydrocarbons, the homologues differ from each other by multiples of (CH_2) .

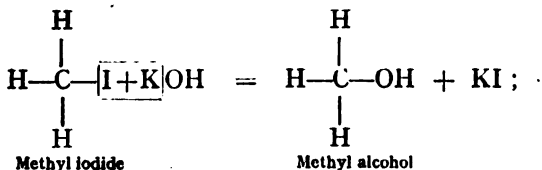
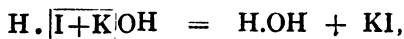
Replacement of Hydrogen by Alkyl Radicles.—In addition to the halogenated derivatives of hydrocarbons, organic substances containing other elements can be prepared; and these, indeed, constitute by far the most important classes of organic compounds.

For instance, oxygen can readily be caused to unite with carbon atoms in organic compounds. Thus if we treat methyl iodide with moist silver oxide, or with aqueous alkali hydroxides, we obtain a product of which the analysis corresponds to the formula CH_4O . As carbon is quadrivalent, oxygen bivalent,

and hydrogen univalent, the only possible mode of formulating this substance is :

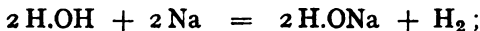


where an oxygen atom is directly attached to the carbon atom. The reaction above indicated proceeds along lines parallel to the reaction between hydrogen iodide and a metallic hydroxide :

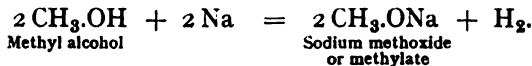


so that this new product—termed an **alcohol**—may be regarded as water in which one of the hydrogen atoms has been replaced by a methyl (CH_3-) group. And indeed in its chemical behaviour it closely resembles water, with of course the difference that only one hydrogen atom is available for reactions.

For instance, on treating water with metallic sodium, hydrogen and sodium hydroxide are produced :

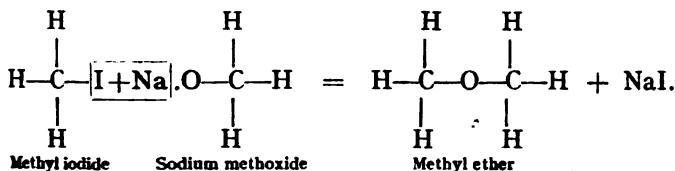
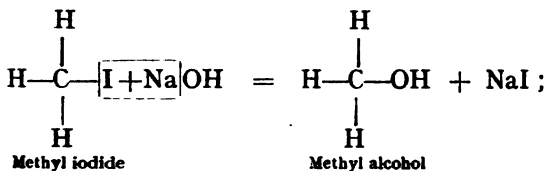


in the same way, sodium reacts with an alcohol, yielding hydrogen and a sodium *alkoxide* (*alkylate*, or *alcoholate*) :



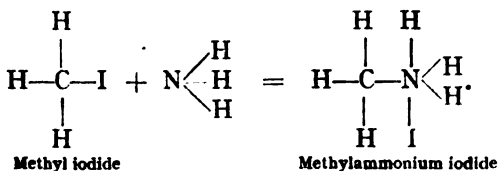
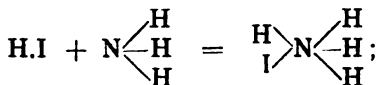
Similarly, just as sodium hydroxide reacts with an alkyl halide to produce a substance in which one hydrogen atom of water is replaced, so does a metallic alkoxide react with a

halogen derivative of a hydrocarbon, producing a derivative of water in which both hydrogen atoms are replaced by carbon radicles :



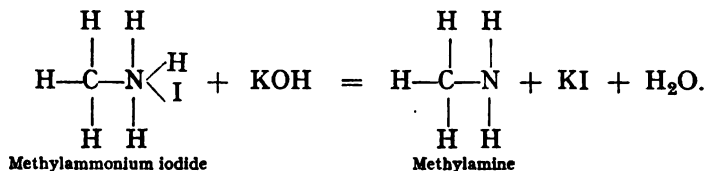
Such a compound is termed an **ether**.

Just as methyl alcohol may be regarded as water in which a methyl group replaces one of the hydrogen atoms, so can we prepare a carbon-containing derivative of ammonia by the replacement of one of the hydrogen atoms in the ammonia molecule by an alkyl group. Like the hydrogen halides, alkyl halides react with ammonia, forming salts of quinquevalent nitrogen :

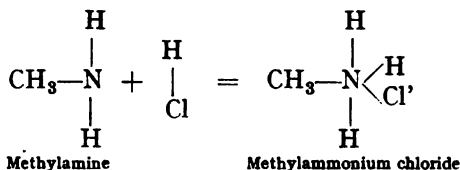


Such a salt may be decomposed by alkali in the same way as an ammonium salt, but in this case a base is formed which is not ammonia, and contains carbon. This is an **amine**, in which a

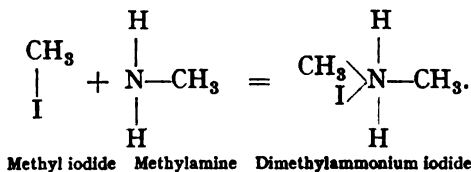
hydrogen atom of ammonia has been replaced by an alkyl radicle :



Such an amine is a strong base closely resembling ammonia, and combines with halogen halides :



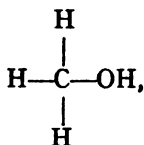
but differs from ammonia in much the same way as an alcohol differs from water. It reacts with further alkyl halide, yielding a derivative of ammonium halide in which a second atom of hydrogen is replaced by an alkyl group :



By repeating this process, all the hydrogen atoms in ammonia—and indeed in an ammonium salt—may be successively replaced by alkyl groups.

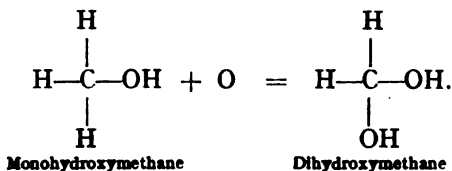
A further example, showing how alkyl groups may replace the hydrogen atoms in the hydrides of elements, is afforded by the action of alkyl halides upon the sulphides and hydro-sulphides of the alkali metals. Just as hydrogen halides decompose such alkali sulphides with formation of hydrogen sulphide, so do alkyl halides react with these substances to produce mono- and di-alkyl derivatives of hydrogen sulphide,

but a more direct method is afforded by treatment of the first member, methyl alcohol :

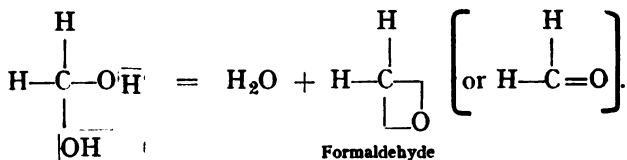


with oxidising agents.

The first step is effected by the catalytic oxidation of methyl alcohol by oxygen in presence of spongy platinum, or by the action of warm copper oxide :

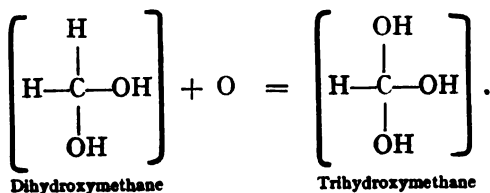


This product, dihydroxymethane, is unstable, and forthwith loses the elements of water, yielding a compound containing doubly bound oxygen ; this is **formaldehyde** :

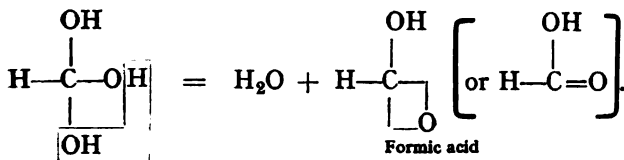


This is the simplest example of the type of compound containing the *carbonyl* group $>\text{C}=\text{O}$.

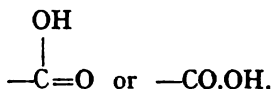
On treatment of formaldehyde with mild oxidising agents, a third hydrogen atom is replaced by hydroxyl :



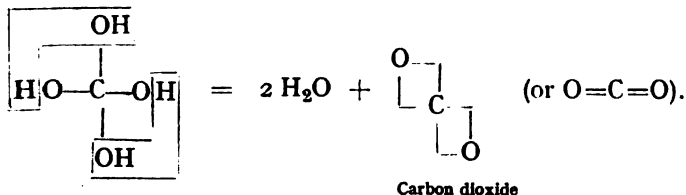
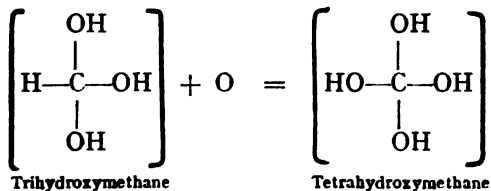
Trihydroxymethane cannot retain two of these hydroxyl groups, and loses the elements of water in the sense of the equation :



The compound, **formic acid**, thus produced, possesses marked acidic properties, and is the simplest member of the large series of organic acids containing the *carboxyl* group :



On further treatment with oxidising agents, we obtain the invariable end-product of the oxidation of organic compounds : **carbon dioxide**. This results in a similar manner from the loss of two molecules of water from carbon tetrahydroxide :



We thus see the progressive replacement of hydrogen atoms in methane by hydroxyl groups ; although the successive substitution is masked by supplementary reactions, it forms an exact parallel to that afforded by the progressive action of chlorine upon methane.

Nomenclature.—Before passing on to a consideration of the other types of organic compounds, it may be well to make clear the nomenclature of the simpler aliphatic hydrocarbons and their immediate derivatives.

In the paraffin series, after the first four members, the names are derived from the corresponding Greek or Latin numerals :

CH_4	Methane	C_6H_{14}	Hexane
C_2H_6	Ethane	C_7H_{16}	Heptane
C_3H_8	Propane	C_8H_{18}	Octane
C_4H_{10}	Butane	C_9H_{20}	Nonane
C_5H_{12}	Pentane	$\text{C}_{10}\text{H}_{22}$	Decane

etc.

In the ethylene series, a similar system is adopted, the suffix “-ylene” replacing the suffix “-ane” in the paraffin series :

C_2H_4	Ethylene	C_5H_{10}	Amylene
C_3H_6	Propylene	C_6H_{12}	Hexylene
C_4H_8	Butylene	C_7H_{14}	Heptylene etc.

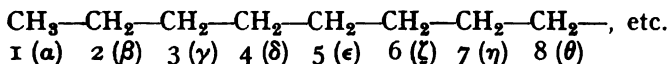
In the acetylene series, the systematic names end with “-ine” :

C_2H_2	Acetylene (or Ethine)	
C_3H_4	Allylene (or Propine)	
C_4H_6	Butinene (or Butine)	etc.

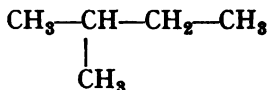
These substances are often described as derivatives of acetylene ; thus allylene may be termed “methyl-acetylene.”

It is further to be noted that, as has already been hinted, the straight chain compounds are termed *normal*, and this is indicated by placing the letter “n-” before the name. Thus normal butane is written “n-butane.” When the chain is branched, the general practice is to employ the prefix “iso,” though in systematic usage the name is derived from the longest normal chain in the compound, the name of the side-chain being quoted with the number (or Greek letter) corresponding

to the position of the carbon atom to which it is attached. Thus :



In this way, isopentane



مثبت بکبر الیہ

is termed "2-methyl butane" or "β-methyl butane." This example should be sufficient to render the system clear.

The alcohols, and the corresponding alkyl halides, are named from the alkyl radicles or groups to which the hydroxyl group or halogen atom is attached :

$\text{C}_2\text{H}_5\text{.OH}$	Ethyl alcohol
$\text{C}_2\text{H}_5\text{.Cl}$	Ethyl chloride
$\text{C}_2\text{H}_5\text{.I}$	Ethyl iodide

The names of the alkyl radicles are derived from those of the hydrocarbons by replacing the suffix "-ane" by "-yl" (the one exception being, as in the ethylene series, the radicle corresponding to pentane) :

$\text{CH}_3\text{---}$	Methyl	$\text{C}_6\text{H}_{13}\text{---}$	Hexyl
$\text{C}_2\text{H}_5\text{---}$	Ethyl	$\text{C}_7\text{H}_{15}\text{---}$	Heptyl
$\text{C}_3\text{H}_7\text{---}$	Propyl	$\text{C}_8\text{H}_{17}\text{---}$	Octyl
$\text{C}_4\text{H}_9\text{---}$	Butyl	$\text{C}_9\text{H}_{19}\text{---}$	Nonyl
$\text{C}_5\text{H}_{11}\text{---}$	Amyl	$\text{C}_{10}\text{H}_{21}\text{---}$	Decyl etc.

The names of the acids and aldehydes differ from those of the corresponding hydrocarbons :

H.COOH	Formic acid	H.CHO	Formaldehyde
$\text{CH}_3\text{.COOH}$	Acetic acid	$\text{CH}_3\text{.CHO}$	Acetaldehyde
$\text{C}_2\text{H}_5\text{.COOH}$	Propionic acid	$\text{C}_2\text{H}_5\text{.CHO}$	Propionaldehyde
$\text{C}_3\text{H}_7\text{.COOH}$	Butyric acid	$\text{C}_3\text{H}_7\text{.CHO}$	Butyraldehyde
$\text{C}_4\text{H}_9\text{.COOH}$	Valerianic acid	$\text{C}_4\text{H}_9\text{.CHO}$	Valeraldehyde
$\text{C}_5\text{H}_{11}\text{.COOH}$	Capric acid	$\text{C}_5\text{H}_{11}\text{.CHO}$	Capraldehyde etc.

Finally, the names of derivatives (which as yet have not been discussed) in which the residue of a fatty acid, after subtracting the hydroxyl group, behaves as a radicle, are derived from those of the acids in a manner similar to those of the alkyl radicles :

H.CO— Formyl
CH₃.CO— Acetyl
C₂H₅.CO— Propionyl
C₃H₇.CO— Butyryl etc.

CHAPTER II

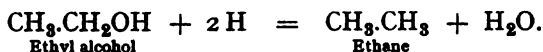
CLASSES OF COMPOUNDS DERIVED FROM ETHYL ALCOHOL

A GENERAL understanding of some of the principal types of organic compounds may be obtained from a study of the reactions of ethyl alcohol and the more important classes of compounds derived from it.

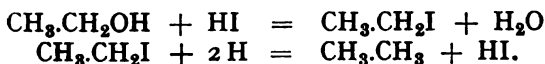
The chief types of reaction which we can apply to ethyl alcohol are reduction, oxidation, dehydration, and esterification. By *reduction* is understood the treatment of a substance in such wise that the percentage of hydrogen in the end-product is greater than that in the original compound. The term *oxidation* implies the formation of an end-product relatively poorer in hydrogen, either by the direct removal of hydrogen from the substance, or by the addition of oxygen, with or without removal of hydrogen from the compound. By *dehydration* we understand the removal of the elements of water from a substance, so that the final product differs from the original. Dehydration may take place either in a single molecule or between two or more, in which latter case the reaction is sometimes termed *condensation*. *Esterification* is a particular type of condensation, in which the hydrogen atom of a mineral or organic acid and the hydroxyl (—OH) group of an alcohol unite with formation of water, while the remaining portions of the two molecules combine to produce an ester or ethereal salt.

Ethyl alcohol can be reduced, with great difficulty, to the corresponding hydrocarbon by heating with phosphonium iodide, which, when heated, decomposes with evolution of

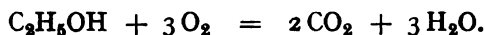
hydrogen ; the nascent hydrogen thus formed acts as a powerful reducing agent :



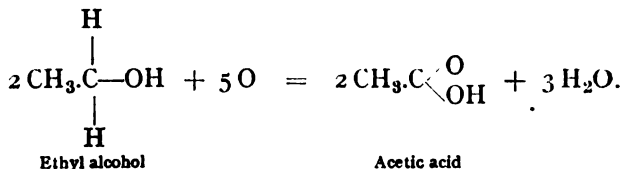
It is probable that ethyl iodide is formed as an intermediate product :



Oxidation may be carried out so as to produce different end-products, according to the method employed. The most violent method of oxidation—heating to a high temperature in presence of oxygen—leads to a complete breakdown of the molecule :

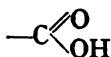


This process, if a sufficiently high temperature be employed, leads with all compounds which contain carbon and hydrogen to the same result, the formation of carbon dioxide and water. It forms the basis of the quantitative estimation of carbon and hydrogen in organic compounds (p. 54). Strong oxidising agents (such as potassium permanganate in alkaline solution), which do not cause entire disruption of the molecule, lead to the formation of a substance possessing acid properties. This is **acetic acid** :



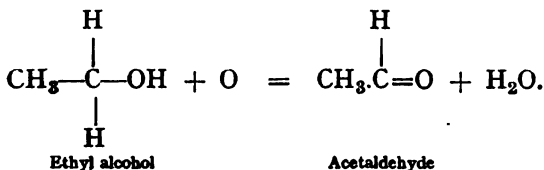
Acetic acid is a typical example of the class of carboxylic acids, which form the most strongly acid series of organic compounds containing only carbon, hydrogen and oxygen. Whilst it is sufficiently powerful to liberate carbonic acid from carbonates, it is a weaker acid (*i.e.* dissociated to a less degree in aqueous

solution) than the majority of mineral acids, such as sulphuric, hydrochloric, or nitric. The carboxyl group

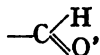


is usually written $-\text{CO.OH}$ or $-\text{COOH}$.

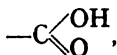
If milder oxidising agents be employed, especially those, such as chromic acid, which react in acid solution, the oxidation is arrested at an earlier stage, **acetaldehyde** being produced :



Acetaldehyde, containing the aldehydic radicle : ?



exhibits no acid properties. Aldehydes are far less stable than the corresponding carboxylic acids, in which the hydrogen atom is replaced by a hydroxyl group :

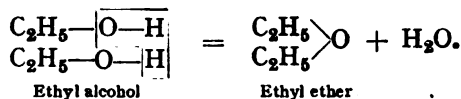


and behave in some measure as unsaturated bodies.

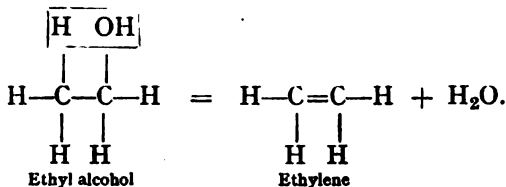
Short of complete oxidation of ethyl alcohol to carbon dioxide and water, no derivative of ethyl alcohol other than acetaldehyde and acetic acid can be prepared by direct oxidation. It will be observed that the methyl ($-\text{CH}_3$) group present in ethyl alcohol remains unattacked by ordinary oxidising agents. This is a general rule. Carbon atoms to which only hydrogen or carbon atoms are attached are not readily oxidised by the reagents usually employed by the organic chemist.

Dehydration of ethyl alcohol may take place in two ways, according to the conditions of the method employed. When the vapour of alcohol is passed over finely-divided aluminium

oxide at 250–260°, the elements of water are removed, with formation of water-vapour and **ethyl ether** :

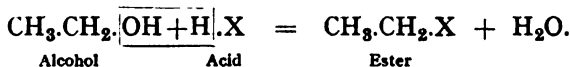


If, on the other hand, the temperature of the alumina be raised to above 260°, more profound dehydration takes place : all the oxygen present in the alcohol is eliminated in the form of water, resulting in the production of the unsaturated hydrocarbon **ethylene** :

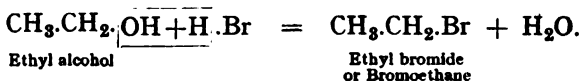


The aluminium oxide does not enter into the reaction. It forms a “contact agent” for the catalytic removal of water.

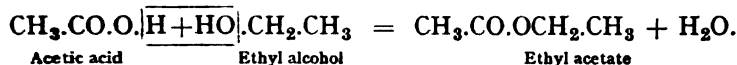
On treatment of alcohol with organic and inorganic acids under suitable conditions, elimination of water ensues, the ethyl group of the alcohol replacing the hydrogen atom of the acid. This may be expressed by the following general equation :



The general term for such an end-product is **ester**. This reaction can take place with halogen hydracids, with inorganic hydroxylic acids, such as sulphuric acid, and with organic carboxylic acids, such as acetic acid. The esters of the halogen hydracids (hydrochloric, hydrobromic, hydriodic acids) are identical with the alkyl halides produced by replacing one hydrogen atom of hydrocarbons by halogen ; for example :



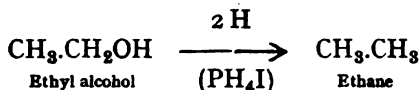
The most general type of ester met with in organic chemistry is the condensation product of an alcohol and an organic acid :



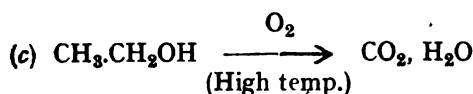
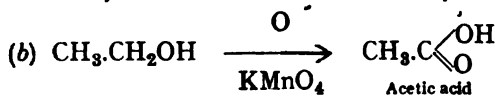
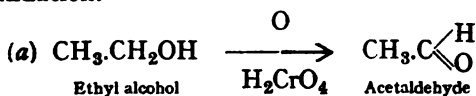
There is, however, only little resemblance in chemical characters between alkyl halides and alkyl esters of carboxylic acids. The main points of difference will be discussed in a later chapter (p. 192).

We may thus summarise the various types of reaction by which we may obtain new products directly from ethyl alcohol :

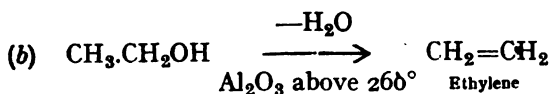
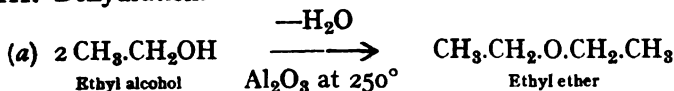
I. Reduction.



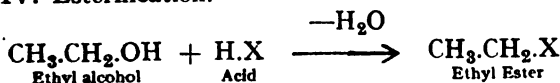
II. Oxidation.



III. Dehydration.

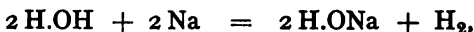


IV. Esterification.

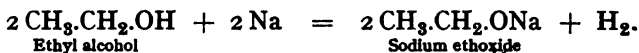


* Prepared by ...

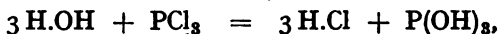
Alcohols, as we have seen, may be regarded as water in which one of the hydrogen atoms is replaced by an alkyl group. They react with all the reagents which decompose water. Thus the alkali metals, which react with water, with evolution of hydrogen and formation of alkali hydroxide :



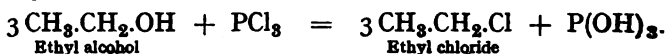
react with alcohol, giving rise to hydrogen and alkali alkoxide :



In the same way, just as phosphorus trichloride and similar compounds react with water to form hydrogen chloride and phosphorous acid :



so do alcohols interact with phosphorus trichloride, giving rise to alkyl chlorides :

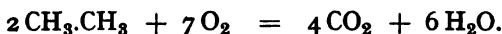


We may now consider the reactions of the various products obtainable from ethyl alcohol by the above method.

The saturated hydrocarbons formed by reduction of alcohols are colourless substances which are almost entirely insoluble in water, and react with ordinary reagents either not at all or with great difficulty.

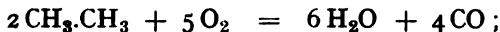
The action of reducing agents is entirely without effect ; since all four valencies of every carbon atom are attached either to hydrogen or to carbon atoms, no further hydrogenation is possible.

Oxidation is, as a general rule, effected only by the most violent methods ; on heating with an excess of oxygen to a high temperature, ethane is completely converted into carbon dioxide and water :



On heating with a supply of oxygen insufficient for complete oxidation, the hydrogen atoms are first attacked with formation of water, the carbon being either oxidised to carbon monoxide,

or deposited in the elemental state as soot, according to the conditions :

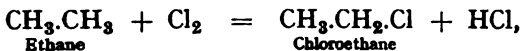


Other violent methods, such as heating to a high temperature under pressure with concentrated nitric acid or sulphuric acid, also lead to the complete oxidation of hydrocarbons.

The halogens react with hydrocarbons in different ways, according to the conditions of experiment. The halogen series: fluorine, chlorine, bromine, and iodine, react with decreasing energy; thus fluorine acts with explosive violence upon methane at as low a temperature as -187° , whilst iodine cannot be induced to react directly with paraffins at all. When a mixture of chlorine and ethane is exposed to ultraviolet light, a violent reaction follows in which the hydrogen combines with chlorine to form hydrogen chloride and carbon is set free :

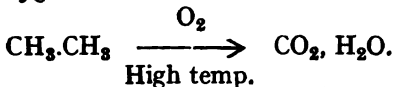


If, however, such a mixture be exposed to diffused daylight, substitution takes place :

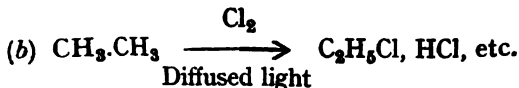
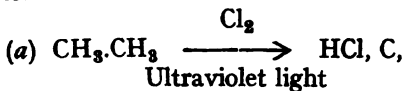


Saturated aliphatic hydrocarbons, taking ethane as typical, can thus react in the following general ways :

I. With oxygen.

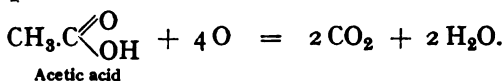


II. With chlorine.

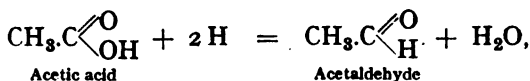


Turning now to the oxidation-products of ethyl alcohol, we may first consider **acetic acid**. This compound, in common with other carboxylic acids, yields a variety of products on treatment with different reagents. Its chief characteristic is its acidic nature, as evidenced by its faculty of forming stable salts with metallic oxides and other bases.

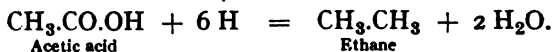
Oxidation is effected only by violent means; this results in the total disruption of the molecule:



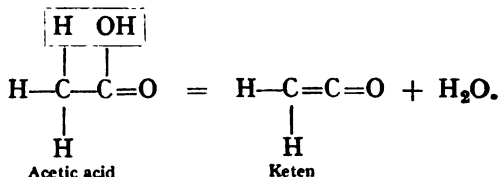
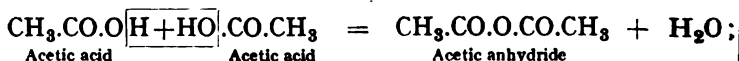
Reduction is brought about with difficulty; nevertheless it is possible by the action of nascent hydrogen to reduce an acid to an aldehyde:



which in turn is readily reduced to the corresponding alcohol (see below). Powerful reducing agents, such as phosphonium iodide, can cause the total reduction of an acid to the corresponding saturated hydrocarbon:



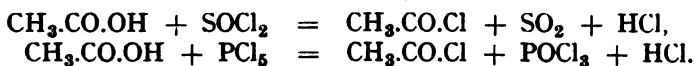
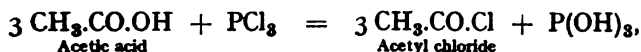
Dehydration can take place in two ways, analogous to the dehydration of ethyl alcohol:



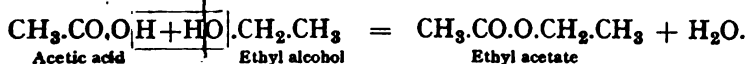
The **acid anhydride** corresponds to ethyl ether; the **keten** to ethylene.

Mineral acids, those containing oxygen as well as the halogen hydracids, are without action upon simple carboxylic

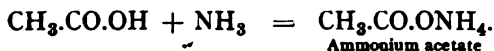
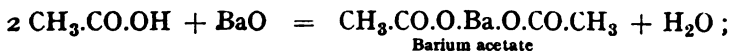
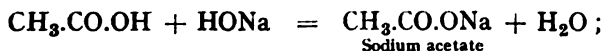
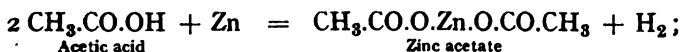
acids. The halides of phosphorus, thionyl chloride, and similar inorganic halogen compounds, convert carboxylic acids into the corresponding **acid halides** :



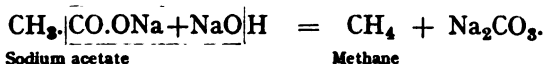
On heating acetic acid with an alcohol, an ester is produced :



Acetic acid, in common with the other carboxylic acids, forms stable salts with metals and with ammonia. Metallic salts may be produced either by the action of a metallic oxide or hydroxide, or even in some cases of a metal itself, upon acetic acid :

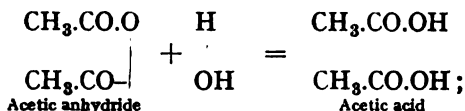


The reactions undergone by heating such salts are of importance. The acetates of the alkali metals may be heated to fusion without decomposition, but if heated with an alkali hydroxide, a carbon atom is eliminated in the form of a carbonate, methane being liberated :

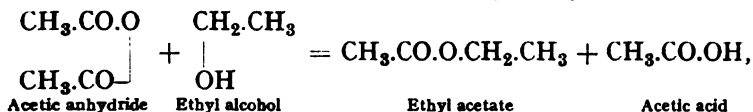


The same effect is produced if the acetates of the alkaline earth metals (Ba, Sr, Ca,) are heated with alkali hydroxides ; but if such a salt be heated by itself, it does not preserve its identity, as do sodium or potassium acetate, but loses the carbonate of the metal with formation of a neutral product

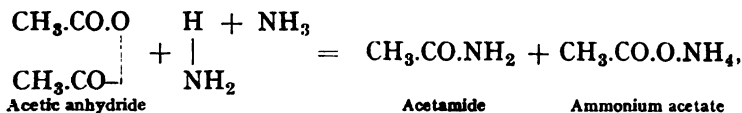
Acid anhydrides behave in a manner similar to acid halides, though with less violence. On boiling with water the free acid is regenerated :



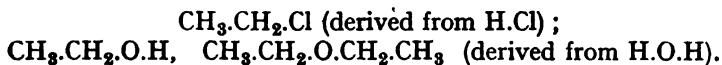
with alcohols they yield the corresponding esters, together with free acid, which esterifies with a further quantity of alcohol :



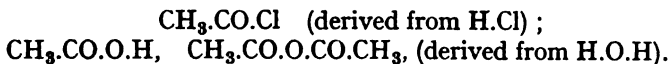
$\text{CH}_3\text{CO.OH} + \text{HO.CH}_2\text{CH}_3 = \text{CH}_3\text{CO.OCH}_2\text{CH}_3 + \text{H}_2\text{O}$;
and with ammonia they yield a mixture of the acid amide and ammonium salt ;



In the previous chapter it was shown how an alkyl radicle (the hypothetical residue of a paraffin hydrocarbon after subtracting one hydrogen atom) can replace a hydrogen atom in the hydrides of elements, thus :



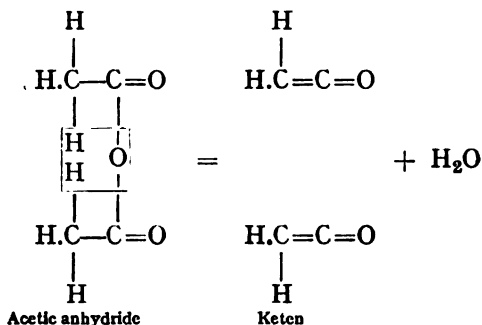
We have now seen that corresponding derivatives may be formed, in which the **acetyl** group $\text{CH}_3\text{CO—}$ functions as the replacing radicle. Thus we have :



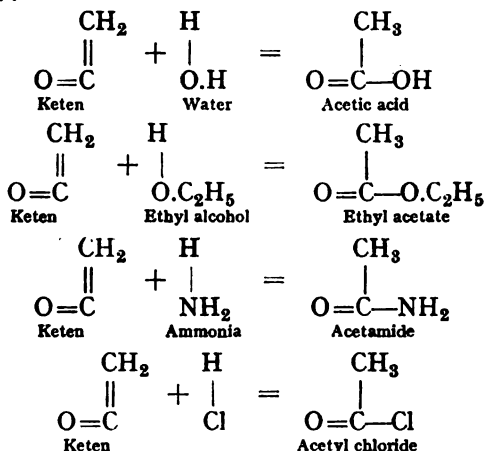
Just as ethyl is a typical *alkyl* radicle, so is acetyl a typical *acyl* radicle. The word "alkyl" is derived from "alcohol," "acyl" in a similar way from "acid."

On treatment with a glowing electric wire, acetic anhydride undergoes decomposition, yielding the second product of

dehydration of acetic acid: **keten**. The reaction may be regarded as parallel to the production of ethylene from ethyl ether (p. 46) :



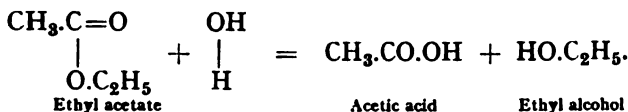
Keten reacts with water, alcohol, ammonia, and hydrogen chloride, forming additive products which are derivatives of acetic acid :



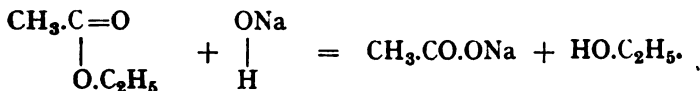
These reactions are all typical examples of *acetylation*, or replacement of a hydrogen atom by an acetyl group.

Esters, which, as has been shown, may be prepared by elimination of water between an acid and an alcohol, are neutral bodies, in accordance with their constitution as ethereal

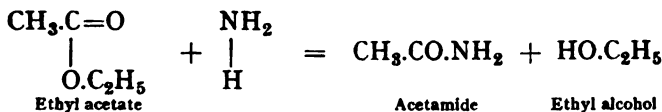
salts. On prolonged boiling with water they are decomposed, yielding the free acid and alcohol :



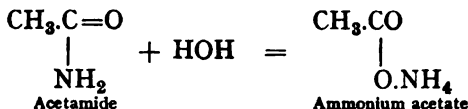
This reaction is termed "saponification" or "hydrolysis," and may be brought about more readily by means of alkalis :



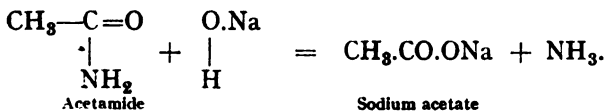
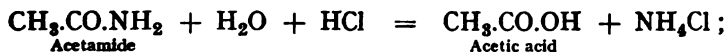
With ammonia, esters yield the corresponding acid amides :



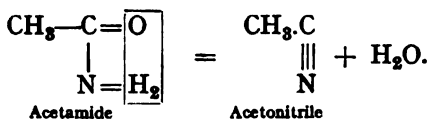
The amides produced, as indicated above, from ammonium salts, acid halides, acid anhydrides, ketens, or esters, can also be hydrolysed by the same methods as esters. On prolonged heating with water they are converted into the corresponding ammonium salts, by the addition of the elements of water :



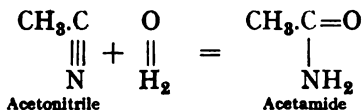
Hydrolysis is effected, however, far more rapidly by boiling with acid or alkaline solutions, salts of ammonia and of the organic acid being formed respectively in the two cases :



On dehydration by the action of phosphorus pentoxide, amides are converted into nitriles, or alkyl cyanides :

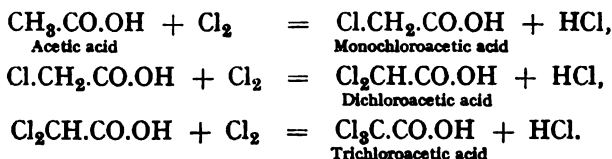


The resultant nitriles may be hydrolysed, yielding different products, according to the violence of the method. On gentle hydrolysis they give rise to acid amides :



whilst more vigorous reagents decompose the amides as fast as they are produced, yielding ammonia and the corresponding carboxylic acids.

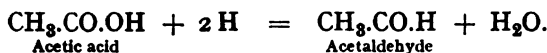
Just as in methane, the hydrogen atoms in acetic acid which are directly attached to carbon may be replaced by hydrogen atoms, yielding mono-, di-, and tri-chloroacetic acids :



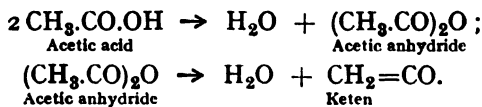
Chlorine has no further effect upon this last product, trichloroacetic acid.

The chief reactions of acetic acid and of its immediate derivatives may now thus be summarised :

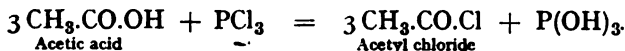
I. Reduction.



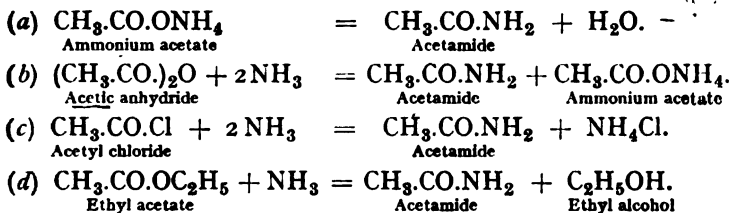
II. Dehydration.



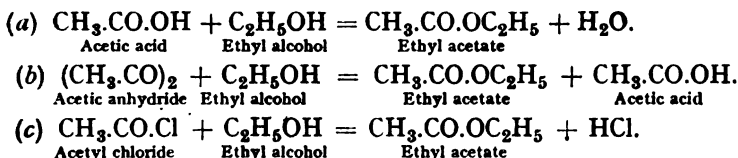
III. Halide formation.



IV. Amide formation.



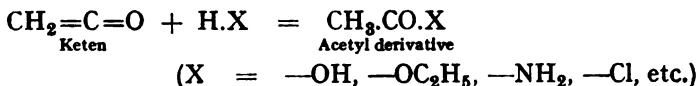
V. Ester formation.



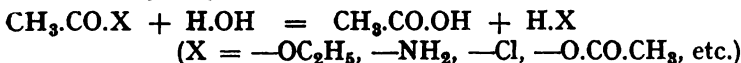
VI. Dehydration of Acetamide.



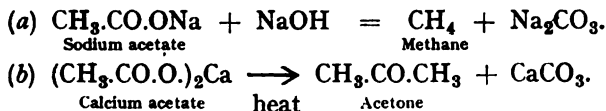
VII. Reactions of Keten.



VIII. Hydrolysis of acetyl derivatives.



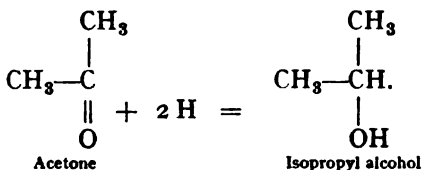
IX. Reactions of salts.



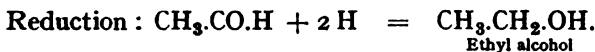
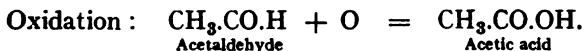
hydrogen atom directly attached to the carbonyl group. On vigorous oxidation, the molecule is broken at the carbonyl group with formation of carboxylic acids ;



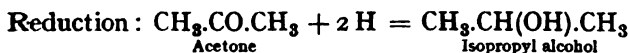
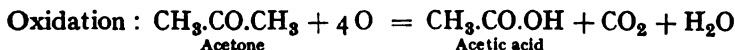
On reduction they yield secondary alcohols, *i.e.* alcohols in which the carbon atom to which the hydroxyl group is attached is itself united to two different carbon atoms :



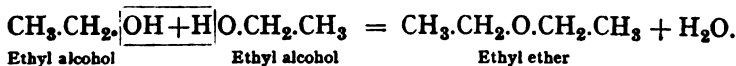
Reactions of Acetaldehyde :



Reactions of Acetone :

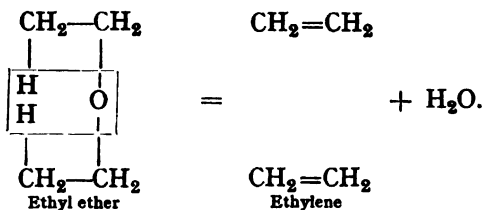


Turning now to the products of dehydration of ethyl alcohol, we have as the first stage diethyl ether (generally termed *ethyl ether*) :

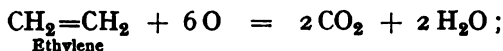


Ethers exhibit but few general reactions, and, more than any other class of compound, resemble in their chemical behaviour the saturated hydrocarbons.

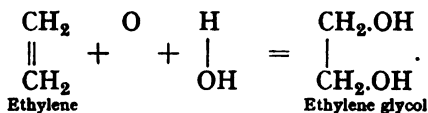
On further dehydration, ethyl ether yields ethylene :



As already indicated, the unsaturated hydrocarbon ethylene is highly reactive ; it is readily attacked by oxidising agents, with disruption of the molecule :

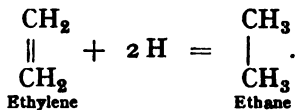


with very mild oxidising agents, oxidation can be effected without rupture, an alcohol containing two hydroxyl groups in the molecule being formed :

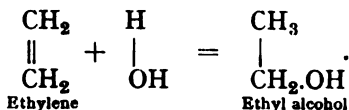


The product, ethylene glycol, will be dealt with later (p. 127).

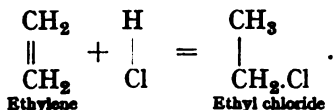
Ethylene can be reduced to ethane by the action of nascent hydrogen :



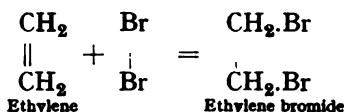
It can also, by an indirect process, be made to take up the elements of water, yielding ethyl alcohol :



Similarly, on treatment with hydrogen halides, ethyl halides are formed :

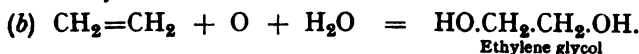
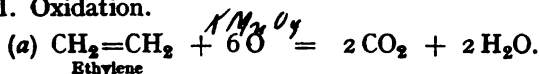


Just as a molecule of ethylene can take up two atoms of hydrogen, so can it absorb, with even more readiness, two atoms of halogen. Thus with bromine *ethylene bromide* results :

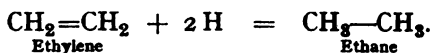


Reactions of Ethylene :

I. Oxidation.



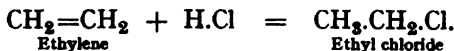
II. Reduction.



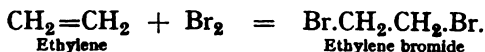
III. Addition of water.



IV. Addition of Hydrogen Halide.



V. Addition of Halogen.



From the above brief survey of some of the more important classes of compound which we have shown to be derived from ethyl alcohol, a preliminary acquaintance with the formulation and reactions of organic substances has been obtained. The student should now be in a position to comprehend the more

CHAPTER III

METHODS OF PURIFICATION AND ANALYSIS

BEFORE discussing in fuller detail the relations and properties of the different classes of organic compounds, attention must be directed to an important practical aspect of organic chemistry. Given an organic substance, what methods are employed to determine its empirical composition? For until this primary question is answered, speculation as to the *constitution*, or relation which the various atoms bear to one another in the molecule, is fruitless.

PURIFICATION

The first point to establish is that of homogeneity. Before further examining an organic substance, we must be certain that we are dealing with a single chemical entity; for were this not the case, not only should we obtain valueless analytical data, but we should observe reactions which do not correspond with the substance which we wish to examine, and thus be led into hopeless confusion.

If the substance can be boiled without decomposition, it is submitted to *distillation*. In this operation the liquid is boiled in a flask fitted with a side-tube attached to a condenser, water-jacketed if the boiling-point be low (Fig. 1), so that the vapour after passing through this side-tube, is condensed again to the liquid state. A thermometer placed in the neck of the flask indicates the temperature of the vapour which passes over. By observing the thermometer, we can collect those portions of the liquid which pass over at constant temperature. When a liquid boils in its entirety at one temperature

(the pressure of course remaining constant), it is in all probability a pure substance ; a constant boiling-point is not only a criterion of homogeneity of a substance, but the temperature at which it boils is a characteristic physical property of a chemical individual.

Some liquids boil at so high a temperature that it is impossible to distil them in the ordinary way without decomposing them. In such a case, distillation under reduced pressure may be the only possible method of purification. The receiver, attached to the end of the condenser by an air-tight join, is

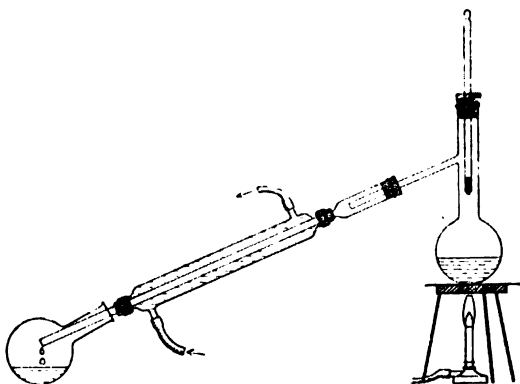


FIG. 1.

fitted with a side-tube connected with a pump and pressure-gauge. Under steady pressure, which must be noted, a pure liquid will boil at constant temperature. The effect of reducing the pressure to about 12 mm. of mercury—which can be done by means of a water-stream suction pump—is to lower the boiling-point of a substance by about 100°C .

Fractional distillation consists in distilling a liquid and separately collecting those portions which boil over successive ranges of temperature ; then redistilling each portion, or *fraction*, until the boiling-point of each is constant. This operation forms the principal method for separating and purifying the components of mixed liquids.

When the substance to be purified is a solid, we resort to *fractional crystallisation*. This is performed by dissolving the substance in some hot liquid in which it is moderately soluble, and filtering off any undissolved impurity. On cooling, crystals of the dissolved substance are deposited, since as a rule a liquid in the boiling state is capable of holding in solution a greater quantity of a substance than in the cold. In this way the less soluble portions are the first to crystallise out, and may be separated by filtration, whilst the more soluble portions remain in solution. If the filtrate be concentrated, a further crop of crystals will separate; this will contain a greater proportion of the more soluble constituent, the filtrate from these crystals being still richer in the more soluble portion. By repeatedly recrystallising the various fractions, the separation of a mixture into its pure components can be effected.

When a crop of crystals appears to be homogeneous (*i.e.* is observed to contain only one kind of crystal when viewed under the microscope), it must be tested for purity. The criterion of purity is the *melting-point*. When the melting-point of a substance remains unchanged after a further recrystallisation, it may be taken as pure, for the reason that the presence of traces of impurity exerts a considerable lowering effect on the temperature at which a substance melts.

The melting-point—an important physical characteristic—is determined by placing a small quantity of the finely powdered substance in a long thin-walled capillary tube, sealed at one end, attaching this to a thermometer so that the substance in the tube lies as closely as possible to the bulb of the thermometer, and immersing this in a bath of sulphuric acid, glycerine, castor oil, or melted paraffin wax, the temperature of which is gradually raised. The point at which the substance melts can readily be determined by continually observing the substance and noting the temperature registered by the thermometer at the moment of melting. It is well to stir the bath, in order to avoid local overheating, which would lead to slight inaccuracies. The substance, if pure, should melt suddenly and completely on attaining the melting-point.

QUALITATIVE TESTS FOR ELEMENTS

Having now satisfied ourselves that the substance is pure, we proceed to ascertain what elements are present in it.

As a first step, a sample is heated in a Bunsen flame on a piece of platinum foil. If it volatilises or burns completely, it is probably not a salt of a metal; if a residue remains, this must be tested qualitatively in order to determine what metal it contains. As a rule, organic salts of the alkali-metal series leave carbonates as a residue; salts of the alkaline earth metals leave a residue consisting of the oxide of a metal. The salts of heavy metals are usually reduced to the metallic condition, and, as in the case of lead, frequently attack the platinum foil. Salts of mercury leave of course no residue.

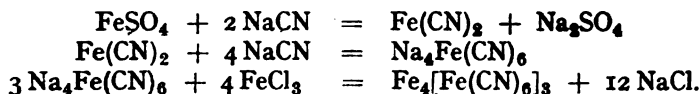
The substance must now be tested for **carbon and hydrogen**. This is done by heating a mixture of the substance with an excess of pure dry copper oxide in a hard-glass tube. By this procedure the carbon is oxidised to carbonic acid, which can be tested by passing the evolved gases through lime-water, whilst the hydrogen yields water, which condenses on the walls of the upper part of the tube.

The presence of **oxygen** cannot be demonstrated by any distinctive test.

The remaining elements for which especial search must be made are nitrogen, the halogens, and sulphur. The presence of these elements can be demonstrated by fusing with sodium or potassium. The substance, if not very volatile, may be heated in a small glass tube with about an equal quantity of metallic sodium (a piece of about the size of a pea is suitable), the mixture being finally heated to redness. If the substance is highly volatile, the best procedure is to heat a piece of sodium (or better, potassium) to redness in a hard-glass tube, and drop the substance upon it in small quantities. In both cases the resultant mass is thrown into a small quantity of distilled water, and the solution so formed is filtered free of charred matter and divided into three portions.

In the first of these we carry out a test for **nitrogen**. If both carbon and nitrogen were present in the original substance,

the effect of the fusion with sodium will have been to form sodium cyanide. The presence of this is shown by the Prussian Blue test:—to one of the portions of the filtrate—which is alkaline owing to the interaction of the excess of sodium with the water—a few drops of dilute ferrous sulphate are added, and the mixture is boiled. By this the cyanide is converted into ferrocyanide; in order to demonstrate its presence, the mixture is acidified, and a drop of dilute ferric chloride is added, whereby ferric ferrocyanide is produced as a blue coloration or precipitate.



In a second portion of the filtrate we carry out a test for **halogens**. The effect of heating a halogen-containing organic substance with sodium is to form sodium halide, so that if no nitrogen has been shown to be present, all we need do is to acidify the solution with dilute nitric acid, and add silver nitrate. If a precipitate be formed, we must ascertain by the routine methods whether it consists of silver chloride, bromide, or iodide. When nitrogen has been found in the original substance, the cyanide present in the filtrate will give rise to a precipitate with silver nitrate, so that in this case the solution after acidification with dilute nitric acid, must be boiled for some minutes in order to expel all cyanide as hydrogen cyanide. After this has been done, silver nitrate is added, and the tests applied as above.

A further test for the halogens consists in heating in a Bunsen flame a small quantity of the substance under examination upon an oxidised copper wire. If halogens be present in the substance, traces of copper halides will be formed; as these are volatile, a green colour will be imparted to the flame.

When **sulphur** is present in the original substance, the effect of heating with sodium is to form sodium sulphide. The presence of sodium sulphide in the solution may often be indicated in the course of the test for cyanide—on adding the ferrous sulphate solution, the precipitate of ferrous hydroxide

is rendered black by the presence of ferrous sulphide. A most delicate test for alkali sulphides is afforded by sodium nitroprusside $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5$, which develops with them a deep violet coloration.

In rare cases **phosphorus** is present in organic compounds. The presence of this element may be shown by fusing the substance with a mixture of sodium carbonate and potassium nitrate, whereby the phosphorus is converted into phosphate, which yields the yellow precipitate of ammonium phosphomolybdate when treated in the routine manner.

QUANTITATIVE ESTIMATION OF ELEMENTS

Carbon and hydrogen are always determined simultaneously in one operation. The principle upon which this analysis is based is the complete oxidation of a known quantity of the organic substance to carbon dioxide and water, which are collected separately and weighed. This is effected as follows: A weighed quantity of the substance, contained in a porcelain boat, is placed in a tube of hard-glass which can be heated to dull redness in a specially constructed furnace consisting essentially of a row of burners. At one end of the tube—the end at which the boat is introduced—a stream of pure dry oxygen can be supplied, at the other end are fitted in series, firstly, a tube containing sulphuric acid or calcium chloride in which the water is absorbed, and then a tube containing concentrated potassium hydroxide, which absorbs the carbon dioxide.

The apparatus is arranged as shown diagrammatically in Fig. 2: at the end A is a stopper with an inlet tube, through which the dry oxygen can enter. B represents a spiral of oxidised copper gauze, which is followed by C, the boat containing the compound to be analysed. DE represents a long column of coarse-grained copper oxide. F represents a space in the tube (see below), followed by a stopper through which passes the tube leading to G, which represents the apparatus for collecting the water, to which is attached H, the apparatus for collecting the carbon dioxide.

At the beginning of the operation, the spiral B and the boat

C are removed, the absorption apparatus G and H disconnected, and the column DE heated to dull redness in a stream of oxygen in order to remove any moisture or organic matter present. The part of the tube A to D remains in the meanwhile cold. When the column of copper oxide is sufficiently hot, the tubes G and H (each of which has previously been accurately weighed) are connected with the combustion tube; the stopper at A is removed, the boat C (containing the weighed substance) is introduced and pushed into position by means of a clean wire or glass rod, the spiral B is pushed in behind it, and the stopper at A is replaced.

A slow stream of dry oxygen is then passed through the entire apparatus (the tube H is fitted with the calcium chloride tube, which prevents loss of moisture due to the passage of the gas through the aqueous potassium hydroxide), and the spiral B is heated. This spiral serves to decompose any vapours of the substance which may distil back against the current of oxygen. The temperature of the substance in the boat C is gradually raised, and the evolved vapours are carried over the hot copper oxide, which completely oxidises them to carbon dioxide and water, being itself reduced to metallic copper. As however there is always an excess of oxygen present, the copper is at once re-oxidised.

In this way the substance is gradually volatilised and burnt. Finally the entire tube is heated to dull redness, and the last traces of carbon dioxide and water are washed out by the stream of oxygen into the absorption apparatus. This is

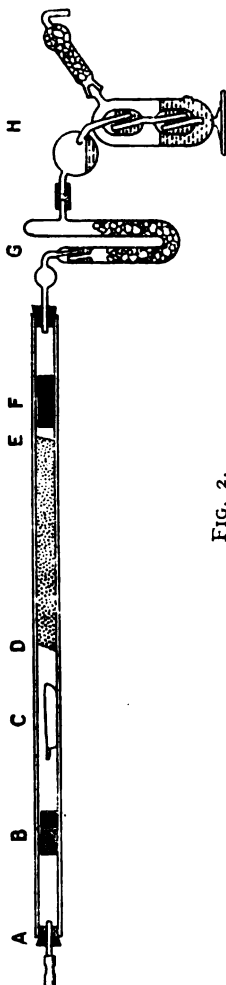


FIG. 2.

then disconnected and weighed: the increase in weight of the sulphuric acid (or calcium chloride) tube shows the amount of water; the increase in weight of the potash bulb shows the amount of carbon dioxide, formed by the combustion of the known amount of substance.

When the compound contains other elements besides carbon, hydrogen or oxygen, certain modifications must be introduced. When nitrogen is present, it is advisable to place a spiral of metallic copper gauze in the unheated portion F of the tube; this has the effect of reducing to elemental nitrogen any oxides of nitrogen, which would otherwise be absorbed by the potash and weighed as carbon dioxide. If halogens be present, a spiral of silver gauze must be placed at F; this will retain any volatile copper halide which may have been formed. When the substance being analysed contains sulphur, lead chromate must be mixed with the copper oxide; this retains all sulphur in the form of lead sulphate.

The calculation of the percentages of carbon and hydrogen from the analytical data is simple. The percentage of carbon in the substance is given by the expression:

$$\frac{\text{Wt. of CO}_2}{\text{Wt. of subst.}} \times \frac{\text{Atomic wt. of C}}{\text{Mol. wt. of CO}_2} \times 100;$$

$$\text{i.e. } \frac{\text{Wt. of CO}_2}{\text{Wt. of subst.}} \times \frac{12}{44} \times 100.$$

The percentage of hydrogen is given by:

$$\frac{\text{Wt. of H}_2\text{O}}{\text{Wt. of subst.}} \times \frac{2 \times \text{At. wt. of H}}{\text{Mol. wt. of H}_2\text{O}} \times 100;$$

$$\text{i.e. } \frac{\text{Wt. of H}_2\text{O}}{\text{Wt. of subst.}} \times \frac{2}{18} \times 100.$$

Nitrogen may be estimated by two distinct methods: (1) that due to Dumas, in which the substance is heated with copper oxide and the nitrogen quantitatively obtained in the elemental state; and (2) that of Kjeldahl, in which the nitrogenous compound is heated with concentrated sulphuric acid, the

nitrogen being thus obtained in the form of ammonia. The Dumas method is applicable to all kinds of nitrogen compounds; the Kjeldahl method can be employed only for derivatives of tervalent nitrogen in which the valencies of the nitrogen atom are attached either to hydrogen or carbon atoms, or for salts of such compounds.

The Dumas method resembles in some particulars the foregoing process of combustion. As before, there is a column of heated copper oxide; the substance, however, is mixed with fine copper oxide, and instead of a stream of oxygen, a stream

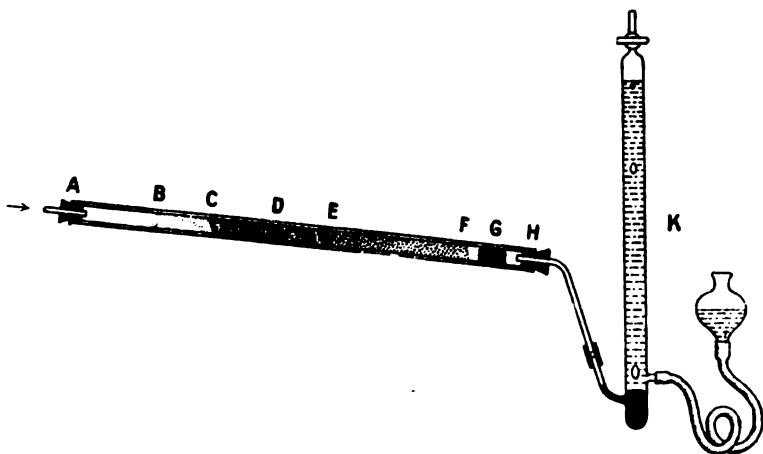


FIG. 3.

of pure carbon dioxide is passed through the apparatus. The materials are disposed in a tube as shown diagrammatically in Fig. 3: at A is a stopper with an inlet tube, through which carbon dioxide can be passed. BC represents a short column of pure fine copper oxide; CD a column of fine copper oxide with which is intimately mixed a weighed quantity of the substance to be analysed; from D to E is a second short column of pure fine copper oxide; EF represents a long column of pure copper oxide in coarse grains. At G is a spiral of carefully reduced copper gauze.

Pure carbon dioxide is introduced at A in a rapid stream, while the column EF is heated nearly to redness. In this way all traces of atmospheric nitrogen are washed out. An azotometer (K), consisting of a vertical column of concentrated (40 per cent.) aqueous potassium hydroxide, arranged as shown in Fig. 3, is then connected at H, so that the gas enters at the bottom of the column. Since the gas consists of pure carbon dioxide, it is completely absorbed as it passes up the column.

The stream of gas entering the combustion tube is now reduced so that it passes very slowly into the azotometer, and the portions of the tube E to D and B to C are heated so that the temperature of the column CB is gradually raised. In this way the carbon contained in the substance is oxidised to carbonic acid, the hydrogen is oxidised to water, whilst the nitrogen is liberated in the elemental condition. Should nevertheless any oxides of nitrogen be formed, these are decomposed by the spiral of metallic copper, yielding copper oxide and nitrogen. The gas passing from the tube into the azotometer thus consists of a mixture of carbon dioxide and nitrogen; the former is entirely absorbed during its passage through the alkali, leaving pure nitrogen, which collects at the top of the column.

When, after having raised the entire tube nearly to dull red heat, the active evolution of nitrogen slackens, a rapid stream of carbon dioxide is passed through the tube, in order to wash out all the nitrogen. The volume of nitrogen can then either be read off directly on the azotometer, neglecting the vapour-pressure of the aqueous potash, or may be transferred into a graduated burette and measured over water, in which case allowance must be made for the vapour-pressure of the water. The temperature and barometric pressure at the time of reading must of course be noted.

In calculating the percentage of nitrogen in a substance, we must first reduce the volume of the gas to N.T.P. (0°C., 760 mm.), allowing, if necessary, for the vapour pressure of the water with which it is in contact. This is given by the expression :

$$\text{Corrected volume at N.T.P.} = \frac{v(B-p) \times 273}{760(273+t)}$$

where v is the observed volume of nitrogen, B the barometric pressure in mm. of mercury, t the observed temperature in degrees C., and p the vapour-pressure of water at the temperature t° . When the nitrogen is measured over 40 per cent. KOH, we assume p equal to zero.

Since 1 cc. of pure nitrogen at N.T.P. weighs 0.0012507 grams, the percentage of nitrogen in the substance is given by :

$$\frac{100}{\text{Wt. of subst.}} \times 0.0012507 \times \text{corrected volume ;}$$

or expressed fully :

$$\frac{100}{\text{Wt. of subst.}} \times 0.0012507 \times \frac{v(B-p) \times 273}{760(273+t)}.$$

In the Kjeldahl process for estimating nitrogen, a weighed quantity (0.1 to 1.0 gram) of the substance is mixed with 25 cc. of pure concentrated sulphuric acid, and the mixture is heated so that the mass darkens in colour and evolves sulphur dioxide. As the reaction proceeds, the temperature is raised until the acid boils gently. This is continued until the colour has disappeared, owing to oxidation of the carbonaceous matter. This oxidation may be accelerated by the addition of a globule of mercury or a crystal of copper sulphate, which substances act as oxygen-carriers in the presence of boiling sulphuric acid.

On completion of the reaction, the mixture is allowed to cool, is diluted with water, transferred to a larger flask, and rendered alkaline by addition of 100 cc. of 40 per cent. sodium hydroxide. The ammonia thus liberated is quantitatively distilled into a measured volume of decinormal sulphuric acid by boiling over one-third to one-half of the bulk of the liquid, after which the excess of standard acid is estimated by titration with decinormal alkali. From the difference in volumes of acid and alkali employed, we can calculate the amount of ammonia distilled over.

Since sulphuric acid is rarely entirely free from ammonia, it is necessary to carry out a blank experiment with the same

quantities of acid and alkali as were employed in the process. The amount of ammonia thus found to have been present in the reagents must be deducted from the total.

The percentage of nitrogen is calculated in the following way :

Let v represent the corrected number of c.c. of decinormal acid neutralised by the ammonia. Then the number of equivalents of ammonia obtained from the weighed amount of substance is equal to $\frac{v}{10,000}$. This corresponds with $\frac{14 \cdot v}{10,000}$ grams of elemental nitrogen, whence the percentage of nitrogen is given by :

$$\frac{100}{\text{Wt. of subst.}} \times \frac{14 \cdot v}{10,000}, \quad \text{i.e.} \quad \frac{14 \times v}{100 \times \text{wt. of subst.}}$$

When estimating the **halogens** and **sulphur**, a weighed quantity of the substance is sealed into a stout-walled glass tube with fuming nitric acid, and heated for some hours at 200–250°. In this way the compound is completely oxidised. This process was devised by Carius and bears his name.

When halogen is to be estimated, a sufficient quantity of finely-powdered silver nitrate is first placed in the tube, which is already sealed at one end, two to three c.c. of fuming nitric acid are added, and the substance, contained in a minute test-tube, is then carefully allowed to fall into the tube, which is thereupon sealed at the other end and heated in a special form of furnace. Silver halide is thus formed, and can be washed out and weighed.

In estimating sulphur, the substance is heated with nitric acid alone, and the sulphuric acid so formed is washed out of the tube and precipitated as barium sulphate.

Care must be exercised in opening the tube, since the formation of carbon dioxide and other gases causes great internal pressure.

Metals in metallic salts are estimated by destruction of the organic portion of the substance and weighing the residue. Salts of alkali metals are evaporated to dryness with a small

quantity of concentrated sulphuric acid, and then heated to bright redness; the residue consists of the sulphate of the alkali metal. Salts of alkaline earth metals are heated alone, oxides or carbonates being obtained, according to the conditions. Salts of certain heavy metals, such as silver, yield the metal in the elemental state when heated.

Having thus outlined the principles of the methods of elementary analysis, we now pass to the deduction of the simplest empirical formula from the analytical data. This can be made clear by concrete examples.

A substance on analysis is found to contain :

Carbon	17.7 per cent.
Hydrogen	9.0 „
Nitrogen	20.8 „
Chlorine	<u>52.5</u> „
	100.0 „

We now divide the percentage number of each element by its atomic weight number; this gives the ratios of the numbers of atoms in the molecule :

Carbon	$17.7 \div 12.0$	$= 1.475$
Hydrogen	$9.0 \div 1.0$	$= 9.000$
Nitrogen	$20.8 \div 14.0$	$= 1.485$
Chlorine	$52.5 \div 35.45$	$= 1.480$

These numbers are then all divided by the smallest of them, whereby it is found that each corresponds, within the limits of experimental error, to an integer :

Carbon	$1.475 \div 1.480$	$= 1.0$
Hydrogen	$9.000 \div 1.480$	$= 6.1$
Nitrogen	$1.485 \div 1.480$	$= 1.0$
Chlorine	$1.480 \div 1.480$	$= 1.0$

The simplest formula for the substance is therefore CH_6NCl ; it may, however, equally well be a polymer $(\text{CH}_6\text{NCl})_n$, where n is any integer.

Another substance, in which only carbon, hydrogen, and silver have been detected, gives on analysis :

Carbon	11.33 per cent.
Hydrogen	0.64 „
Silver	67.90 „
	<hr/>
	79.87 „

The percentages of these three elements do not add up to 100 ; the difference (20.13) must therefore be the percentage of oxygen. Proceeding as before, we have :

Carbon . . .	$11.33 \div 12.0 = 0.944$	$\left. \vphantom{\begin{matrix} 0.944 \\ 0.640 \\ 0.629 \\ 1.259 \end{matrix}} \right\} \div 0.629 =$	$\left\{ \begin{matrix} 1.5 \\ 1.0 \\ 1.0 \\ 2.0 \end{matrix} \right.$
Hydrogen . . .	$0.64 \div 1.0 = 0.640$		
Silver . . .	$67.90 \div 107.9 = 0.629$		
Oxygen . . .	$20.13 \div 16.0 = 1.259$		
	<hr/>		
	100.00		

Since the value which we have here obtained for carbon is not an integer, it must be converted into one ; this can in this case be effected by doubling. We have then :

Carbon	3
Hydrogen	2
Silver	2
Oxygen	4

The simplest empirical formula for this substance is thus $C_3H_2O_4Ag_2$.

The foregoing accounts of the quantitative analytical methods for determining the elements in organic compounds are merely indications of the principles involved ; for a detailed description a text-book of practical organic chemistry must be consulted.

CHAPTER IV

DETERMINATION OF MOLECULAR WEIGHT

By quantitative elementary analysis we are able to deduce the *simplest* empirical formula of a substance ; we cannot, however, be certain whether the true composition is to be expressed by this simplest formula, or by a multiple thereof. To take, as a concrete example, acetic acid ; qualitative analysis demonstrates the presence of only carbon and hydrogen ; quantitative analysis shows these elements to be contained in the percentage proportions :

Carbon	40.0 per cent.
Hydrogen	6.7 „

The remainder, which must consist of oxygen, amounts to 53.3 per cent. These figures lead to the simplest empirical formula CH_2O .

Now we have no guarantee that the properties of acetic acid are best expressed by this formula ; the same analytical figures would be obtained for substances possessing the formulæ CH_2O , $\text{C}_2\text{H}_4\text{O}_2$, $\text{C}_3\text{H}_6\text{O}_3$, etc. ; in short, the analysis of acetic acid leads to the general formula $(\text{CH}_2\text{O})_n$, where n is an unknown integer.

It has frequently been stated that the molecular weight of an organic acid can be determined by ignition of its calcium or silver salt, whereby the percentage of calcium or silver in the salt can be ascertained. This is an error ; what is here determined is not the molecular weight, but the *equivalent weight*.

For example, a silver salt of a carboxylic acid is found to contain 55.9 per cent. of silver ; the remaining 44.1 per cent.

consists of the acidic portion of the molecule. Since 107.9 grams of silver can replace 1.0 gram of hydrogen in an acid, the equivalent weight of the acid is given by x :

$$\begin{array}{l} 55.9 : 44.1 :: 107.9 : x \\ \text{Whence} \qquad \qquad \qquad x = 85.0 \end{array}$$

Elementary analysis of the acid itself (carbon 55.8 per cent., hydrogen 7.0 per cent.) is found to lead to the simplest empirical formula C_2H_3O , the sum of the atomic weights of which amounts to 43 ; but since the equivalent weight was found to be 85, the simplest empirical formula for the silver salt must be $C_4H_5O_2Ag$, corresponding to an acid of formula $C_4H_6O_2$, the molecular weight of which would be 86. But the equivalent of a dibasic acid $C_8H_{12}O_4$ (molecular weight 172) would also be 85, since the acidic portion $C_8H_{10}O_4$ is capable of combining with two atoms of hydrogen or silver : $C_8H_{10}O_4Ag_2$. In short, the molecular weight of an acid whose equivalent is 85 may be any value of the expression $(85 + 1)_n$, where n represents a whole number.

In order to determine the value of n we must resort to a physical method.

According to Avogadro's hypothesis, equal volumes of gases under similar conditions of temperature and pressure contain equal numbers of molecules. Here we have a solution of the problem : if we can determine the relation between the weight and the volume of the vapour of a substance under known conditions, we shall be able to deduce the molecular weight. In other words, the *vapour-density* must be ascertained.

Vapour-density is usually expressed by taking that of hydrogen as a standard of unity ; since the molecular weight of hydrogen is 2, the molecular weight of the compound under examination is given by doubling its vapour-density. Thus the vapour-density of water is 9 (*i.e.* a given volume of steam weighs nine times as much as the same volume of hydrogen under the same conditions), whence the molecular weight of water, *in its gaseous state*, is 18, corresponding with the formula H_2O .

The vapour-density of a compound CH_2O would be 15 [*i.e.*

$\frac{1}{3}(12+2+16)$]; that of $(\text{CH}_2\text{O})_2$ would be 30 $[\frac{2}{3}(12+2+16)]$; that of $(\text{CH}_2\text{O})_3$ would be 45 $[\frac{3}{3}(12+2+16)]$; and so on. Experiment shows that the vapour-density of acetic acid is 30; whence the molecular weight must be 60, corresponding with the formula $(\text{CH}_2\text{O})_2$ or $\text{C}_2\text{H}_4\text{O}_2$.

Unfortunately many organic substances cannot be obtained in the form of vapour—they decompose on being heated to a temperature sufficiently high to volatilise them—so that for such compounds this method is inapplicable. In order to determine the molecular weight of compounds which cannot be examined in the pure gaseous condition, we make use of the fact that the vapour-pressure of a liquid is lowered by a dissolved substance, in proportion to its *molecular concentration*. This lowering of vapour-pressure causes the boiling-point of the liquid to rise, and the freezing-point to fall, likewise proportionately to the number of molecules of solute present in unit volume of solution; so that by noting the elevation of boiling-point and depression of freezing-point of a known volume of liquid containing a known weight of dissolved substance, we can calculate the molecular weight of this substance.

We may now consider in principle the chief methods by which the molecular weight is estimated.

VAPOUR-DENSITY DETERMINATION

Of widest applicability is the method of **Victor Meyer**. The principle of this method is the following: a known weight of the substance is allowed to fall into a vessel heated above its boiling-point; by its expansion air is displaced. This air is collected and measured.

In the apparatus, shown diagrammatically in Fig. 4, the bulb B is jacketed with the vapour of some substance boiling in the bath A. The side-tube C passes into a water trough D, in which a graduated tube E is placed, in order to collect the air expelled through C. At the head of the tube is joined an arrangement F, resembling a large stop-cock, for supporting the tube containing the weighed amount of the substance, and for allowing this to fall into B when desired. The substance

F

is contained in a loosely stoppered bottle or tube, small enough

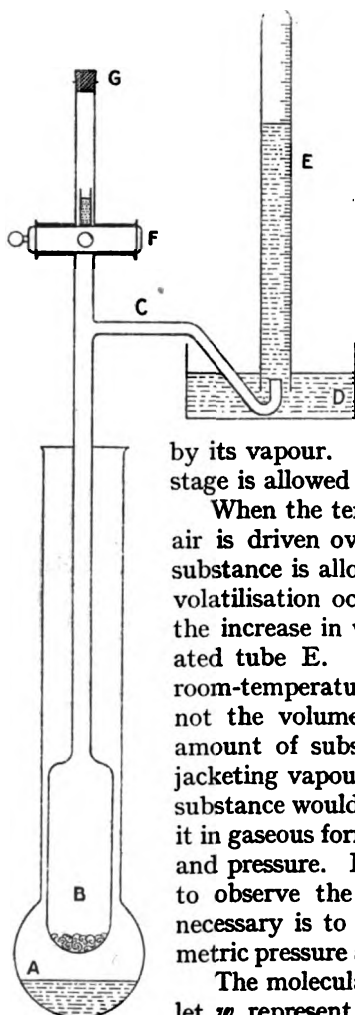


FIG. 4.

of diameter to pass through the bore of the stop-cock at F. It is introduced at the open upper end G of the tube, which is then stoppered. When released, the bottle falls upon a layer of glass-wool or asbestos in the bulb B, which serves to prevent the walls of the vessel from being broken by its impact.

The liquid of the jacket A (the boiling-point of which must lie about 40° above that of the substance) is heated so that the bulb B is completely surrounded by its vapour. Any air which is expelled at this stage is allowed to escape without entering E.

When the temperature is constant, no further air is driven over, and the bottle containing the substance is allowed to fall from F to B. Rapid volatilisation occurs, and the air driven over by the increase in volume is collected in the graduated tube E. Since this air is cooled to the room-temperature during its passage, it represents not the volume of the vapour of the weighed amount of substance at the temperature of the jacketing vapour at A, but the volume which the substance would occupy were it possible to obtain it in gaseous form at the atmospheric temperature and pressure. For this reason it is not necessary to observe the temperature of B; all that is necessary is to note the temperature and barometric pressure at the time of reading the volume.

The molecular weight is calculated as follows: let w represent the weight of the substance in grams, and V the observed volume (in c.c.) of air driven over, this being measured at a temperature t under

barometric pressure B . We must firstly calculate from the observed volume of air the column which it would occupy, in the dry state, at 0° and 760 mm. pressure: from the barometric pressure we must deduct the vapour pressure of water at t° ; let this be called p ; the volume v of the air reduced to 0° and 760 mm. (*i.e.* N.T.P., =normal temperature and pressure) is given by:

$$v = V \times \frac{273}{273 + t} \times \frac{B - p}{760}$$

Now 1 c.c of hydrogen at N.T.P. weighs 0.0000896 grams, so that an equal volume of pure hydrogen would weigh 0.0000896.v grams. The weight of substance was w grams, so that the vapour-density D of the substance (compared to hydrogen) is:

$$D = \frac{w}{0.0000896.v}$$

The molecular weight $M(=2D)$, is thus given by the total expression:

$$M = \frac{2 \times 760 \times w(273 + t)}{0.0000896 \times 273 \times V(B - p)}, \quad \text{i.e.} \quad \frac{62140 \times w(273 + t)}{V(B - p)}$$

The method of **Dumas** is classic, but is now rarely employed. A clean dry glass bulb with a narrow neck drawn out to a fine point is first accurately weighed, the temperature and atmospheric pressure being noted. Some of the substance (in the liquid state) is now sucked into it by warming the bulb and allowing it to cool while the nozzle is immersed in the liquid. The entire bulb, with the exception of the end of the neck, is then immersed in a bath heated to a temperature lying about 40° above the boiling-point of the liquid. The contents of the bulb thus boil rapidly, and in so doing expel all the air, leaving the pure vapour of the substance. When no further liquid remains, the temperature of the bath and the barometric pressure are noted, and the tip of the neck sealed with a small flame. The sealed bulb is then dried and again weighed, again noting temperature and pressure.

In order to determine the volume of the bulb, the tip of the neck is cut off under cold water, whereby the water enters and completely fills the bulb. When constant temperature is reached, the bulb is weighed. From the difference in weight between the bulb empty and full of water, the volume can be calculated by reference to the density of water at the temperature at which it was filled.

Knowing now the volume of the bulb, we can calculate the density of the vapour at the temperature of the bath and under the observed atmospheric pressure, since we have determined the weight of the bulb, filled firstly with air at a known temperature and pressure, and then filled with the vapour of the substance. The two weighings must be corrected, if necessary, for the buoyancy in the air at the times of weighing; this will, however, be necessary only if the temperature and barometric pressure differ widely at the two times of weighing. As this is improbable, it may generally be assumed that this factor can be neglected.

The calculation is carried out thus: let A represent the observed weight of the bulb full of air, B the weight of the bulb containing the vapour of the substance, C the weight of the bulb full of water.

Representing as D , the density of water at the temperature at which the bulb was filled, then the volume (V) of the bulb is given by:

$$V = \frac{C - A}{D}$$

Now 1 c.c. of dry air at N.T.P. weighs 0.001293 grams; the weight (a) of V c.c. of air at t° and under P mm. is therefore given by:

$$a = 0.001293 \times V \times \frac{273}{273 + t} \times \frac{P}{760}$$

The weight of the bulb alone is $A - a$; the weight of the vapour (w) is therefore given by:

$$w = B - A + a.$$

Representing the temperature of the bath by t , and the barometric pressure by P , then the volume (v) of the vapour, corrected to N.T.P., is:

$$v = V \times \frac{273}{273 + t} \times \frac{P}{760}$$

This volume corresponds to w grams of the vapour, so that 1 c.c. of vapour at N.T.P. weighs $\frac{w}{v}$ grams.

Now 1 c.c. of hydrogen at N.T.P. weighs 0.0000896 grams; the density (D) of the vapour (as compared with hydrogen) is therefore:

$$D = \frac{w}{0.0000896.v}$$

the molecular weight being equal to twice this expression.

A third method, that of **Hofmann**, consists in allowing a weighed quantity of substance to volatilise in the space above a mercury barometer column, jacketed at known constant temperature, and noting the increase in volume and change in pressure. In this

way, the vapour-density can be very accurately determined, but the manipulations are difficult and the calculation tedious. Hence its employment is, as a rule, restricted to those cases in which the vapour of the substance is unstable under atmospheric pressure, but stable under reduced pressure.

DETERMINATION OF MOLECULAR WEIGHT BY SOLUTION METHODS

Elevation of boiling-point of solutions.—When any substance is dissolved in a liquid, it is found that the solution must, in order to cause it to boil, be heated to a higher temperature than is the case with the pure solvent. In dilute solutions it is found that the degree of elevation of the boiling-point is directly proportional to the *number of molecules* of substance dissolved in unit volume, entirely without reference to its molecular weight.

The boiling-point of a known quantity of a solvent is accordingly noted on a thermometer of special construction, devised by Beckmann, which has a scale of narrow limits, but is of great sensitiveness, and which can be set to any desired range of temperature by adding or removing mercury to the column.

The construction of this instrument is shown in Fig. 5. In order to set this thermometer, the bulb B is warmed until the thread of mercury reaches the mercury in the reservoir A; the bulb is then immersed in a bath at a temperature of the upper limit, and the thread of mercury separated from the remainder in the reservoir by gently tapping the head of the thermometer.

The solvent is boiled in a specially constructed vessel which ensures ebullition at constant temperature and is jacketed with the vapour of the same liquid in order to prevent loss of heat by radiation. A reflux condenser returns the condensed vapour to the vessel. The bulb of the thermometer is totally immersed in the boiling liquid.

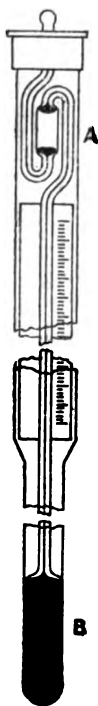


FIG. 5

After carefully noting the temperature, a weighed amount of the substance is added to the boiling solvent, and the change in the temperature of the boiling liquid is noted.

Although the elevation of the boiling-point is independent of the nature of the dissolved substance, it varies with different solvents. Every liquid has its own "molecular elevation," this being a constant characteristic for the solvent. This constant, C , is defined as the number of degrees by which the boiling-point of 100 grams of solvent is raised by the addition of one gram-molecule of solute (dissolved substance). Liquids employed as solvents are :

	C .		C .
Water	5.2	Ethyl Acetate . .	26.1
Methyl Alcohol .	9.2	Benzene	26.7
Ethyl Alcohol .	11.5	Phenol	30.4
Acetone	16.7	Aniline	32.2
Ethyl Ether . .	21.1	Chloroform . . .	36.6
Carbon Disulphide	23.7	Carbon Tetrachloride	48.0
Acetic Acid . .	25.3	Ethylene Bromide	63.2

Thus if we dissolve $\frac{1}{100}$ gram-molecule, *i.e.* 1.300 grams, of glucose (mol. wt. = 130) in 100 grams of water, the boiling-point will be raised by 0.052° . Similarly the addition of 2.420 grams of cane sugar (mol. wt. = 242) to 100 grams of water would raise the boiling-point by 0.052° . If 100 grams of methyl alcohol were employed as the solvent, the elevation would be 0.092° .

The molecular weight of an unknown substance is calculated as follows : Let w represent the weight of substance added, W the weight of solvent, t the observed elevation of boiling-point, C the constant for the liquid, and M the unknown molecular weight of the substance :

M grams of solute in 100 grams of solvent raise B.P. by C degrees.

$$\therefore w \quad \text{,,} \quad \text{,,} \quad W \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{100.w.C}{W.M} \quad \text{,,}$$

$$\text{But } \frac{100.w.C}{W.M} = t$$

$$\text{Whence } M = \frac{100.w.C}{W.t}.$$

This method involves certain experimental difficulties ; chief among the disadvantages in the tendency of the temperature to fluctuate, owing to slight irregularities in heating. It is therefore preferable, when possible, to employ the following method.

Depression of freezing-point of solutions.—Just as the boiling-point of a liquid is elevated to an extent proportional to the number of molecules dissolved therein, so is the freezing-point of a liquid depressed in proportion to the molecular concentration of a dissolved substance.

The procedure is similar to that described above : a weighed amount of solvent is contained in a tube of special construction, jacketed with an air-bath surrounded by another bath the temperature of which lies about two degrees below the freezing-point of the liquid. The solution is allowed to cool slowly, with continual stirring, until crystals of solid solvent begin to separate. The temperature of the liquid, which remains constant at this point, is read on a Beckmann thermometer supported in the liquid.

The tube containing the liquid is then removed from the air-bath and gently warmed until all the solid has again melted ; a weighed quantity of the substance is added through the side-tube and the freezing-point of the solution determined in the same way.

The depression of freezing-point of a liquid depends exclusively upon the *molecular concentration* of the solute, being independent of the nature or molecular weight of the latter ; as in the elevation of boiling-point, the *molecular depression* is a constant characteristic for the solvent. Liquids commonly employed are :

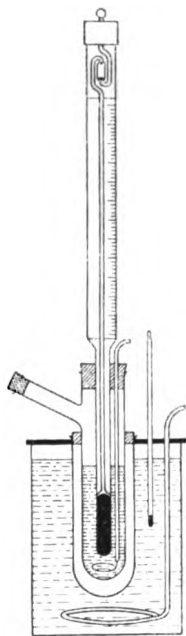


FIG. 6.

	C.		C.
Water	19	Nitrobenzene . .	71
Formic Acid . .	28	Phenol	72
Acetic Acid . .	39	Diphenylamine .	88
Benzene	50	Ethylene Bromide	118
Naphthalene . .	69	Bromoform . .	143

The molecular constant C is defined as the depression (in degrees Centigrade) of the freezing-point of 100 grams of solvent on addition of one gram-molecule of solute.

The molecular weight of the solute is deduced by exactly the same process of reasoning as in the method of elevation of boiling-point: Let w represent the weight of solute, W the weight of solvent, t the observed depression of freezing-point, and C the constant for the liquid; then the molecular weight M is given by the expression:

$$M = \frac{100.w.C}{W.t}.$$

None of the methods commonly employed by the organic chemist for the determination of molecular weight are of great accuracy; as a rule they furnish results correct to within about one or two per cent. It is not necessary that greater accuracy than this should be obtained, for the sole purpose of such measurements is to enable a decision to be made between the different multiples of the simplest empirical formula. To recall the case of acetic acid already quoted, elementary analysis leads to the formula $(CH_2O)_n$, the different values of which may be 30, 60, 90, 120, and so on, according to the value of n . It will be seen that only an approximate value is necessary in order to be able to assign the correct formula to the compound.

It must here be pointed out that solutions of electrolytes in dissociating media, as for instance salts in water, lead to anomalous results, since the dissociated ions independently depress the freezing-point, or raise the boiling-point, to the same extent as whole undissociated molecules.

CHAPTER V

HYDROCARBONS

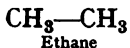
THE name Hydrocarbon is given to all compounds containing only carbon and hydrogen. It may be said that upon them is based the entire edifice of organic chemistry, since all organic compounds can be regarded as derivations of hydrocarbons formed by replacing hydrogen atoms by other atoms or groups. In this way, the simplest of all hydrocarbons—carbon tetra-hydride, or methane, CH_4 —is the primal substance from which the many thousands of organic compounds may be traced.

In point of purely chemical interest they are relatively unimportant; nevertheless, by virtue of their character as the backbone of organic chemistry, their theoretical significance cannot be too strongly emphasised.

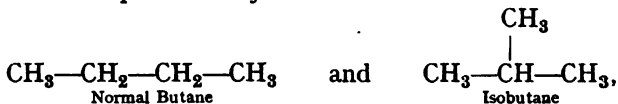
SATURATED HYDROCARBONS

The saturated hydrocarbons or **paraffins** are compounds of carbon and hydrogen, the composition of all of which is expressible by the general formula $\text{C}_n\text{H}_{2n+2}$. Thus the first member, methane, which contains one carbon atom in the molecule, possesses the composition $\text{C}_1\text{H}_{(2 \times 1) + 2}$ or CH_4 . The composition of ethane, which contains two atoms of carbon, is expressed by $\text{C}_2\text{H}_{(2 \times 2) + 2}$ or C_2H_6 . Analysis of the third member, propane, leads to the formula C_3H_8 , which corresponds with $\text{C}_3\text{H}_{(2 \times 3) + 2}$. And so on. These hydrocarbons are homologues, each differing from the preceding member by the increment CH_2 . We have seen that, assuming the constant

quadrivalency of carbon and univalency of hydrogen, their formula can be written only according to the scheme :



The next member of the series, butane, C_4H_{10} , may be written in two possible ways :



and it is found that there are in fact two distinct hydrocarbons whose composition can be expressed by C_4H_{10} . These two compounds thus possess identical *composition* and different *constitution*.

With increasing number of carbon atoms in the molecule, the number of isomers increases rapidly. The following table shows the number of possible isomers for the various stages in the ascending scale of paraffin hydrocarbons :—

Formula.	Number of Isomers.	Formula.	Number of Isomers.
C_4H_{10}	2	C_9H_{20}	35
C_5H_{12}	3	$\text{C}_{10}\text{H}_{22}$	75
C_6H_{14}	5	$\text{C}_{11}\text{H}_{24}$	159
C_7H_{16}	9	$\text{C}_{12}\text{H}_{26}$	355
C_8H_{18}	18	$\text{C}_{13}\text{H}_{28}$	1855

Mixtures of paraffin hydrocarbons occur naturally in great quantity, principally as the petroleum deposits of Eastern Europe and North America. The lower members constitute a large proportion of the "natural gas" often existing in conjunction with petroleum in the United States. They also appear in many coal mines as "fire-damp." Methane occurs, as already stated, among the products of fermentation of vegetable matter in marshes and the sediment of ponds.

Crude petroleum, which exists, often under considerable pressure, in the shale-enclosed "oil wells," consists of a mixture of hydrocarbons which can be partially separated by fractional distillation. After being pumped to the surface it is distilled.

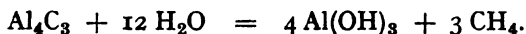
Owing to the highly inflammable nature of the more volatile paraffin hydrocarbons, it is essential that the petroleum employed for lamps should be carefully standardised. All kerosene must

therefore pass the "flash-point" test. This is carried out by gradually raising the temperature of a sample of the oil and noting at what point vapour is evolved with rapidity sufficient to allow it to be ignited by a free flame placed from time to time momentarily near the surface of the liquid.

Solid hydrocarbons occur in Galicia and elsewhere as *Ozokerite*, a white waxy solid. This product is largely employed for the manufacture of candles.

MODES OF FORMATION OF PARAFFIN HYDROCARBONS

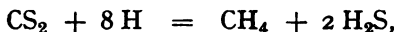
From the elements.—It has long been known that traces of hydrocarbons are produced by the action of mineral acids upon carboniferous iron. Moissan, by a study of the action of metals upon carbon in the electric furnace, was able to show that the carbides so produced yielded hydrocarbons on decomposition with water or acids. Thus aluminium carbide, on treatment with water, yields methane :



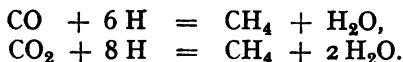
Methane was first synthesised by Berthelot, by passing a mixture of carbon disulphide and hydrogen sulphide over heated copper :



It can also be prepared by the reduction of carbon disulphide by means of phosphonium iodide :

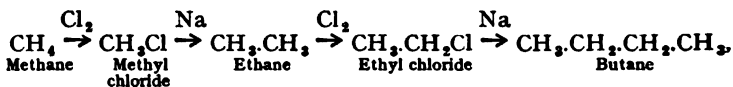


or by the reduction of the oxides of carbon by means of hydrogen in presence of finely-divided nickel at temperatures between 250° and 400° (see below) :



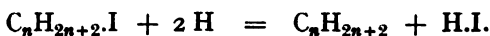
The same reaction can also be brought about by the action of the electric spark discharge upon a mixture of carbon monoxide and hydrogen.

From methane we can pass to the higher members by treatment of the halogen derivatives with a metal :

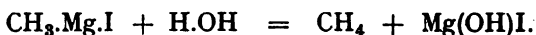


and thus we can, by a series of such steps, synthesise these more complicated compounds from the elements.

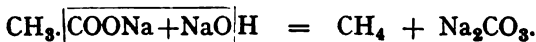
From organic substances.—Alkyl halides, especially the iodo derivatives of hydrocarbons, may be reduced by such agents as the copper-zinc couple (zinc coated with metallic copper) in alcoholic solution in presence of mineral acid :



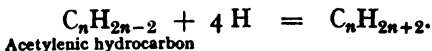
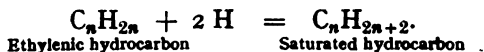
A general method of wide applicability is the treatment of an alkyl magnesium halide (p. 235) with water :



By distillation of the salt of a carboxylic acid and an alkali metal with soda lime, the elements of carbon dioxide are split off in the form of alkali carbonate, yielding a hydrocarbon containing one carbon atom less in the molecule :

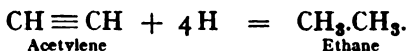
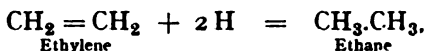


Further, paraffin hydrocarbons can be produced by the reduction of unsaturated hydrocarbons (see below). This is readily effected by employment of nascent hydrogen or of hydrogen in presence of a contact (or catalytic) agent :



The catalytic agents which are generally employed are either finely-divided nickel at a temperature between 90° and 300°, aqueous solutions of colloidal palladium or platinum, or platinum-black, in an atmosphere of hydrogen, under pressure if necessary. The metal first occludes hydrogen, with which it then parts so as to hydrogenate the unsaturated compound.

Examples of such reductions are :



As already stated, simple alkyl halides can be made to yield more complex hydrocarbons by elimination of halogen. This may be effected by treatment of a dry ethereal solution of the halide with sodium (Wurtz reaction) :



Magnesium or zinc may also be employed, in which case the reaction takes place in two or more stages (see pp. 234, 235).

GENERAL PHYSICAL AND CHEMICAL PROPERTIES OF SATURATED HYDROCARBONS

Paraffin hydrocarbons are colourless and insoluble—or very sparingly soluble—in water. The lowest members of this series—those containing one to four carbon atoms in the molecule—exist in the gaseous form under the usual atmospheric conditions. The normal, or straight-chain, members containing five to fifteen carbon atoms are liquids; those containing sixteen and more carbon atoms are solids of comparatively low melting-point. As a general rule, the boiling-points of hydrocarbons, and indeed of all organic compounds in homologous series, rise with increase in molecular weight.

The specific gravity at ordinary temperature of all the members in the liquid or solid states is less than that of water.

They react, as already stated, with extreme reluctance. Those containing four and more carbon atoms burn in the air with a luminous and often smoky flame.

Among the isomers of each stage in the series, the following rules, which also hold good for many other classes of compounds, may be enunciated :

(1) The normal straight-chain isomer possesses the highest boiling-point.

(2) The boiling-point of isomers decreases with the number of side-chains.

(3) Among isomers containing equal numbers of side-chains, those possessing the greater symmetry of structure possess the higher boiling-points.

INDIVIDUAL MEMBERS

The following list shows the first five normal or straight-chain hydrocarbons of the paraffin series :

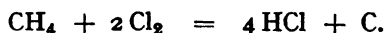
		Boiling-point.
Methane	CH_4	-164°
Ethane	$\text{CH}_3\cdot\text{CH}_3$	-84°
Propane	$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3$	-44°
<i>n</i> -Butane	$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	$+1^\circ$
<i>n</i> -Pentane	$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	$+36^\circ$

The chemical properties and methods of preparation of the first members may be taken as typical of the remainder ; it is unnecessary for the student to know more than the existence of the subsequent members and their relation one to the other.

Methane is a colourless, odourless gas, which can be condensed to a mobile liquid which boils under atmospheric pressure at -164° . At a lower temperature it solidifies to a white crystalline mass which melts at -184° . It is most conveniently prepared either by reduction of methyl iodide by means of coppered zinc in presence of dilute alcoholic sulphuric acid, or by heating a mixture of dry sodium acetate, potassium hydroxide, and quicklime. It may be collected over water.

It is very slowly oxidised on shaking with a solution of potassium permanganate. The higher normal members of the series containing three to five carbon atoms are scarcely attacked by this reagent.

On treatment with chlorine in diffused daylight in the cold, substitution takes place, chloro-derivatives being formed (see p. 94). In presence of sunlight the reaction follows a different course, yielding hydrogen chloride and free carbon with explosive violence :



Ethane may be prepared in the same way as methane, by treatment of ethyl iodide with coppered zinc in acid solution. It melts at -172° and boils at -84° under atmospheric pressure.

Propane may be prepared in the same way from *n*-propyl iodide or isopropyl iodide. It melts at -45° and boils under atmospheric pressure at -44° .

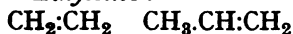
UNSATURATED HYDROCARBONS

Ethylene Series

The hydrocarbons of this series may exist in several types. Chief in importance are the simple ethylenes, containing one "double bond," expressible of the general formula C_nH_{2n} , where the integer *n* is greater than unity.

Such are :

Ethylenes :

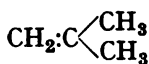


Ethylene

Propylene



Butylenes



Isobutylene

Unsaturated hydrocarbons can also exist which contain more than one double linkage. Examples of these are *allene* and *butadiene* :



Allene



Butadiene

We have already discussed some of the reasons for formulating ethylenic compounds with a double linkage and for postulating the persistency of the quadrivalency of carbon. Nevertheless it must be borne in mind that most simple ethylenic compounds behave as if they contained atoms of lower valency which eagerly seek an opportunity of attaining their higher valence. Further it must be pointed out that a double bond is by no means twice as strong as a simple bond ; on the contrary, a molecule may be torn asunder at the double linkage by means of reagents which leave the corresponding saturated compound intact.

Ethylenic hydrocarbons do not occur in nature in the same abundance as saturated hydrocarbons. They form a

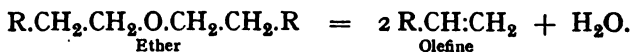
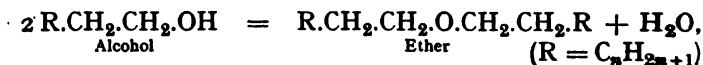
constituent of Galician petroleum, but do not appear in the American oil. They are more frequently found in plant life : for example, the turpentine family consists principally of complex ethylenic hydrocarbons.

MODES OF FORMATION OF ETHYLENIC HYDROCARBONS

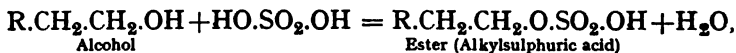
Ethylenic hydrocarbons, also called *olefines* or *alkylenes*, are produced by destructive distillation of many organic compounds of more complicated structure. Thus ethylene forms one of the illuminating constituents of coal gas.

General methods of preparation of individual members are :

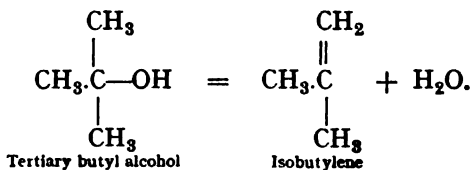
Dehydration of Alcohols.—(1) Dehydration of alcohols or ethers by means of catalytic agents such as heated metallic oxides :



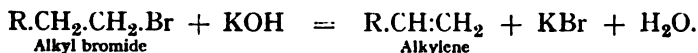
(2) Dehydration of alcohols by means of hot concentrated sulphuric acid or orthophosphoric acid, in which reactions esters are formed as intermediate products :



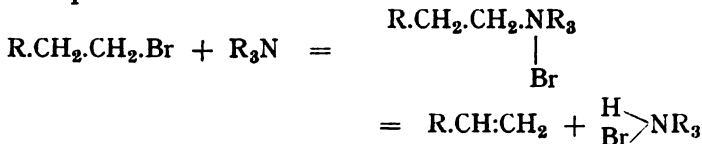
(3) Dehydration of alcohols by means of such reagents as zinc chloride. Secondary and tertiary alcohols can also be dehydrated by these methods ; in fact, they yield the corresponding ethylenes rather more readily than do primary alcohols :



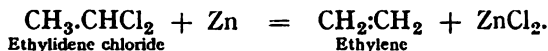
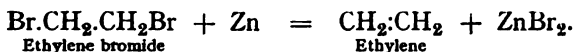
Removal of hydrogen halide from alkyl halides.—(1) By boiling with alcoholic potash :



(2) By heating with certain tertiary amines ; in which reaction quaternary ammonium salts are produced as intermediate products :



Removal of halogen from dihalogen compounds.—This is readily effected by warming the substance in alcoholic solution with zinc dust or coppered zinc :



Reduction of acetylenes.—This can be brought about by partial hydrogenation :

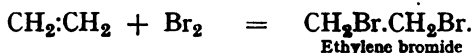
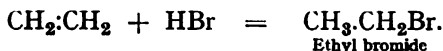
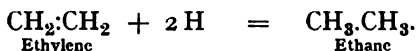


GENERAL PHYSICAL AND CHEMICAL PROPERTIES OF ETHYLENIC HYDROCARBONS

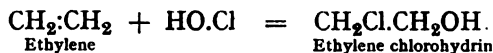
Ethylenic hydrocarbons are colourless, insoluble in water, and of lower specific gravity, in the liquid and solid states, than water. In most of their physical properties they closely resemble the paraffins—thus, members of the series containing four and less atoms of carbon in the molecule are gases at ordinary temperatures.

In chemical properties they are distinguished by extreme

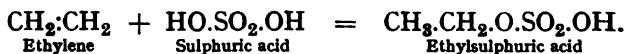
reactivity. They readily yield, as seen above, addition-products with hydrogen, with hydrogen halides, with halogens :



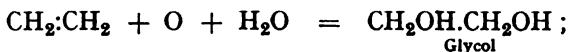
With hypochlorous acid and hypobromous acid, chlorohydrins and bromohydrins (see p. 128) are produced :



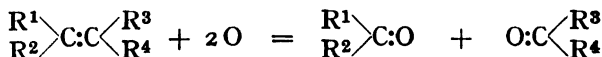
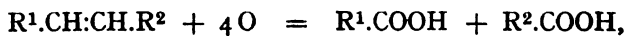
Ethylenes react with concentrated sulphuric acid with formation of alkylsulphuric acids (p. 195) :



With oxidising agents they can be either converted by gentle oxidation into glycols (dihydroxylic alcohols, p. 127) :

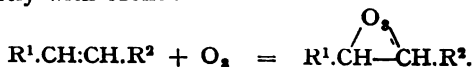


or, by more forcible methods, the molecule is broken at the double linkage, with formation of more highly oxygenated products :

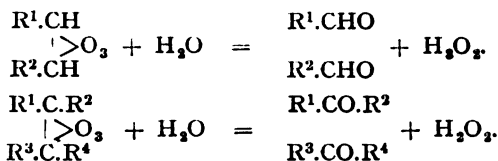


(where R^1 , R^2 , etc., are alkyl radicles).

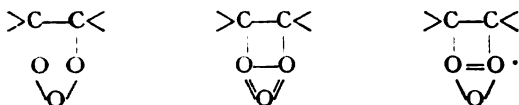
An important property of ethylenic compounds is that of uniting directly with ozone :



These products, termed *ozonides*, are decomposed on treatment with hot water into aldehydes or ketones and hydrogen peroxide :



By taking advantage of this property, and identifying the decomposition products, the position of double bonds in unsaturated compounds has been established. Such ozonides are generally glassy solids which decline to crystallise, and are frequently explosively unstable. Their structure is as yet undetermined ; the following formulæ have been proposed :



Finally, ethylenes may be polymerised in presence of contact agents such as zinc chloride, or by the action of the silent electric discharge, with formation of more or less complex polymers.

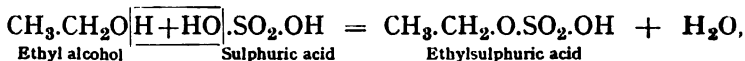
INDIVIDUAL MEMBERS

		Boiling-point.
Ethylene	. . . CH ₂ :CH ₂	-103°
Propylene	. . . CH ₃ .CH:CH ₂	- 48°
Butylene (1)	. . . CH ₃ .CH ₂ .CH:CH ₂	- 5°
Butylene (2)	. . . CH ₃ .CH:CH.CH ₃	+ 1°
Isobutylene	. . . CH ₃ .C(CH ₃):CH ₂	- 6°

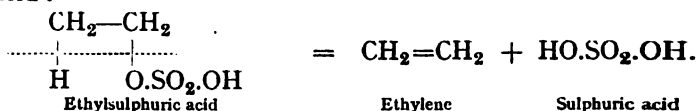
Ethylene CH₂=CH₂ is a colourless gas, possessing a faint but characteristic odour ; it liquefies under atmospheric pressure, at about -103°. On further cooling it solidifies to a crystalline mass melting at -169°.

The classic method of preparation consists in heating a mixture of ethyl alcohol with about three times its weight of sulphuric acid, and gradually adding more alcohol to replace that converted into ethylene. The reaction takes place in the

following steps: alcohol and sulphuric acid at first react together to form ethylsulphuric acid:



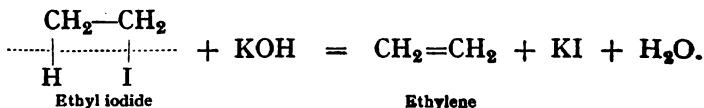
this, on further heating, breaks down into ethylene and sulphuric acid:



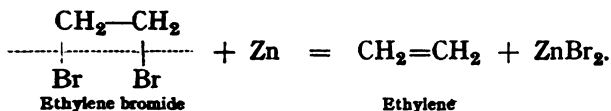
leaving the acid free to react with more alcohol.

This is said to be a "continuous" process, since an unlimited quantity of alcohol may theoretically be dehydrated by a limited amount of sulphuric acid. In practice, however, it is not possible to convert an unlimited amount of alcohol into ethylene with only one charge of sulphuric acid, since certain side-reactions (such as charring) take place, the efficacy of the acid being thereby reduced. It has, however, been found that for all practical purposes a truly continuous process can be achieved by employing orthophosphoric acid in place of sulphuric acid, since this does not evince the same tendency to enter into side-reactions. The acid is maintained at a temperature of 220–240°, and the alcohol is slowly added to it in a continuous stream. This is at once converted into pure ethylene, no charring being observed. In principle this process is identical with the sulphuric acid method, ethylphosphoric acid $\text{CH}_3\text{.CH}_2\text{O.PO(OH)}_2$ being formed, like ethylsulphuric acid, as an intermediate product. An indefinitely large quantity of ethylene may be produced by the use of only 25 cc. of the orthophosphoric acid.

Another method for preparing ethylene is to heat an ethyl halide (p. 98), such as ethyl iodide, with concentrated alcoholic potassium hydroxide. This reaction is a simple elimination of hydrogen halide, comparable to the decomposition of ethylsulphuric acid by heat:



It is also formed by the elimination of bromine from ethylene bromide (p. 104) by means of zinc :



As above stated (p. 32), ethylene can be produced by the catalytic dehydration of ethyl alcohol, the vapour of which is passed over finely-divided aluminium oxide at a high temperature.

Ethylene burns in the air with a luminous flame, and forms an explosive mixture with oxygen.

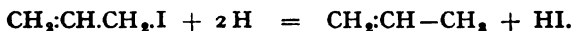
On heating to above 360° , it is decomposed into methane and acetylene :



The acetylene thus formed polymerises with production of complicated hydrocarbons.

The readiness with which it combines with halogens can be seen on mixing equal volumes of ethylene and chlorine or bromine vapour. The colour of the halogen instantly disappears, and the walls of the vessel are bedewed with oily drops of ethylene chloride or bromide.

Propylene $\text{CH}_3\text{CH=CH}_2$ may be prepared by dehydration of normal propyl alcohol or isopropyl alcohol by the methods described for the preparation of ethylene. It is also produced by reduction of allyl bromide $\text{CH}_2\text{:CH.CH}_2\text{Br}$ or allyl iodide $\text{CH}_2\text{:CH.CH}_2\text{I}$ (p. 99) by methods—such as treatment in alcohol solution with coppered zinc—which do not lead to the reduction of double linkages :



It may likewise be prepared by distilling glycerol (p. 130) with zinc dust. The precise course of this reaction is unknown :



Unsaturated hydrocarbons in which two double bonds are situated on the same carbon atom differ somewhat in nature and preparation from other ethylenic compounds. The simplest member, **allene**, is prepared from α,β,γ -tribromopropane (glycerine

tribromohydrin, cf. p. 131) by distillation with solid potash, and subsequently removing bromine from the product by means of zinc dust:



It is a colourless gas at ordinary temperature; it melts at -146° and boils at -32° under atmospheric pressure.

Acetylenic Series

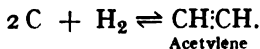
Hydrocarbons of the simple acetylenic series can be expressed by the general formula $\text{C}_n\text{H}_{2n-2}$, where n represents 2 or more. Acetylenic compounds are formulated by a triple bond between two carbon atoms:



The character of the triple linkage differs from the single and the double linkages in many fundamental respects. One of the most important points of comparison is the stability of the molecule. We have seen that saturated hydrocarbons, containing only single bonds, for example ethane, are stable both at high and at low temperatures. Ethylene is stable at low temperatures, but on heating to even a moderately high temperature decomposes into saturated and acetylenic hydrocarbons. Acetylene, on the other hand, is stable at extremely high temperatures, but unstable at low temperatures.

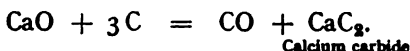
MODES OF FORMATION OF ACETYLENIC HYDROCARBONS

(1) *From the elements.*—Acetylene is produced from an electric arc between carbon poles in an atmosphere of hydrogen. This reaction is a reversible one, in consequence of which an equilibrium mixture of acetylene and hydrogen is produced:

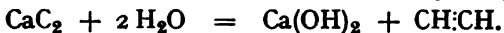


For this reason this mode of formation is of only theoretical interest.

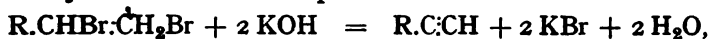
The chief method of preparation is from calcium carbide. An intimate mixture of coke and quicklime, when heated in the electric furnace, is converted into calcium carbide, a gray fusible solid :



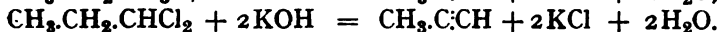
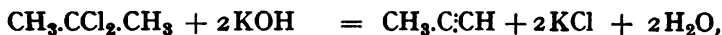
This reacts energetically with water, liberating acetylene :



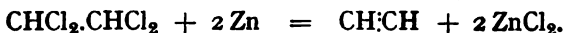
(2) *From organic substances.*—(a) Removal of hydrogen halide. Acetylenes are readily produced by boiling dihalides of ethylenes with alcoholic potash :



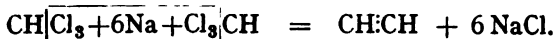
or by a similar treatment of compounds in which two halogen atoms are attached to the same carbon atom :



(b) Removal of halogen.—Acetylenes can be prepared by the action of zinc upon $\alpha.\alpha.\beta.\beta$ -tetrachloro- or tetrabromo-compounds. Symmetrical tetrachloroethane thus yields acetylene :



Acetylenes are also produced by the action of finely divided or heated alkali metals upon $\alpha.\alpha.\alpha$ -tri-halogen-substituted hydrocarbons :

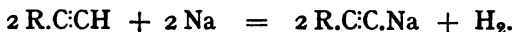


Finally, acetylene is produced by the decomposition at a red heat of many organic substances, such as ethylene, methyl alcohol, ethyl alcohol, and acetaldehyde. It is also formed by the incomplete combustion of many such compounds.

PHYSICAL AND CHEMICAL PROPERTIES OF ACETYLENIC HYDROCARBONS

Like the paraffins and the ethylenes, the lower members form colourless gases which are insoluble in water. They burn in air with a luminous smoky flame.

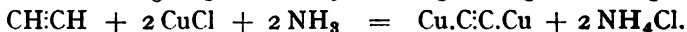
A remarkable property of a triple bond is that it confers weak salt-forming properties upon the carbon atoms which it connects. Thus acetylene and its mono-alkyl derivatives are capable of forming salts with different metals. On treatment of a dry ethereal solution of an acetylene with metallic sodium, hydrogen is evolved, and the sodium salt is formed :



Calcium carbide, which was mentioned as the chief source of acetylene, is thus merely the calcium salt of acetylene :

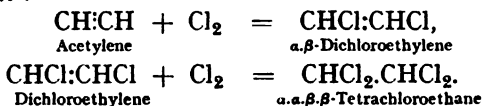


On passing acetylene into ammoniacal solutions of silver and cuprous salts, *acetylides* of these metals are precipitated :

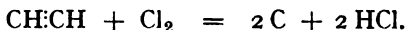


Acetylides of heavy metals are frequently highly explosive in the dry state. Disubstituted acetylenes, in which no hydrogen atom is attached to triply-bound carbon, exhibit no salt-forming properties.

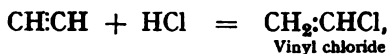
Acetylenes, in accord with their unsaturated character, are capable of combining with hydrogen and with halogens. They do so, however, less eagerly than do the corresponding ethylenes. Chlorine does not react with pure acetylene in the absence of light ; in diffused daylight these gases unite slowly to form α,β -dichloroethylene, which then reacts with more chlorine to form the symmetrical ($\alpha,\alpha,\beta,\beta$ -) *tetrachloroethane*, or *acetylene tetrachloride* :



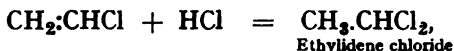
When, however, the acetylene is not perfectly pure, chlorine reacts with explosive violence, yielding carbon and hydrogen chloride (cf. p. 35) :



Similarly, hydrogen halides add on to acetylene, first yielding halogen-substituted ethylenes or vinyl halides (p. 100):

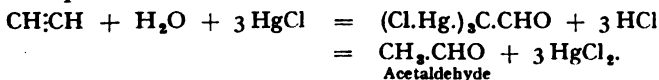


and then ethylidene halides (p. 103):



the second chlorine atom attaching itself to the carbon atom poorer in hydrogen.

The elements of water can also be added on by treating the gas with an acid solution of mercuric chloride, an intermediate mercuric compound being formed, which yields acetaldehyde with the acid present:



INDIVIDUAL MEMBERS

		Boiling-point.
Acetylene	$\text{CH}\cdot\text{CH}$	-82°
Allylene (Methylacetylene)	$\text{CH}\cdot\text{C}\cdot\text{CH}_3$	-23°

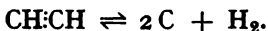
Acetylene, $\text{CH}\cdot\text{CH}$, the prototype and only important member of the series, is a colourless gas, boiling under atmospheric pressure at -82° . The melting-point lies at -81° , or rather higher than the boiling-point under these conditions. Under about 26 atmospheres acetylene forms a mobile liquid boiling at 0° . Owing to the fact that its formation from the elements takes place with absorption of heat—or, in other words, that it is an endothermic compound—it is highly explosive, especially in the liquid state under pressure.

Acetylene, in the crude condition as evolved from calcium carbide, possesses a powerful leek-like odour; this is due to the presence of impurities. When pure it is stated to possess a not unpleasant ethereal odour. Water under ordinary atmospheric conditions dissolves about its own volume of acetylene; the solubility is diminished on saturating the water with salts.

It is chiefly employed for illuminating purposes, being generated by the gradual addition of water to the carbide, so that the gas is

evolved in a constant stream. As it burns in air with a smoky flame when emitted from an ordinary jet, a special burner, in which the flame has access to an increased supply of air, must be employed. Acetylene also finds application in welding processes; for this purpose it is usually burnt in a blowpipe supplied with oxygen.

On heating to a very high temperature it is partially broken down into its constituent elements, the reaction being a reversible one :



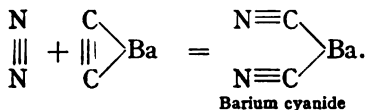
It is readily attacked by oxidising agents. On prolonged action of air in presence of alkali, considerable quantities of acetic acid are produced :



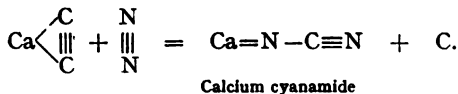
On sparking with nitrogen it yields hydrogen cyanide :



a reaction recalling the formation of barium cyanide by heating barium carbide in a stream of nitrogen (p. 216) :



It is interesting to note the difference in behaviour of calcium carbide when subjected to these conditions (p. 230) :



Acetylene may be quantitatively estimated by bringing it into contact with an ammoniacal solution of cuprous chloride, collecting the precipitate, converting it into copper oxide, and weighing. Cuprous acetylides may be decomposed by warming with dilute hydrochloric acid, or better, with a solution of potassium cyanide :



This forms a convenient method for the preparation of acetylene in a pure state.

CHAPTER VI

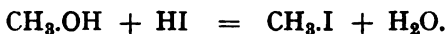
HALOGEN COMPOUNDS

HALOGEN derivatives of hydrocarbons may be regarded either as hydrocarbons in which hydrogen atoms are replaced by halogen atoms, or as esters of halogen hydracids and alkyl radicles. Both points of view should be maintained, as both serve to elucidate the mode of formation and the reactions of this class of bodies.

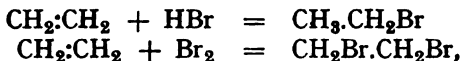
The first conception is exemplified by the chlorination of methane :



the second by the formation of methyl iodide from methyl alcohol and hydriodic acid :



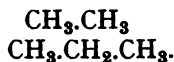
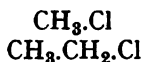
These two processes, together with that of addition, *e.g.* :



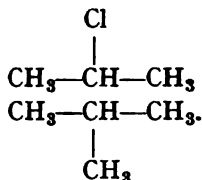
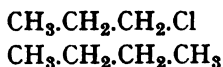
comprise the three main principles underlying the production of organic halogen compounds, and may be described as *substitution*, *addition*, and *esterification*.

In theoretical character the halogen compounds closely resemble the hydrocarbons, with the difference that the possibility of *isomerism* is even greater. To consider for example the mono-chlorinated hydrocarbons: we have but

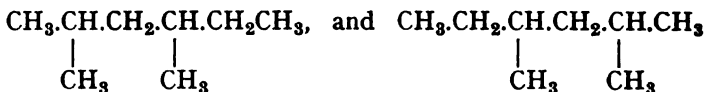
one chloromethane and one chloroethane, just as there can exist only one ethane and one propane :



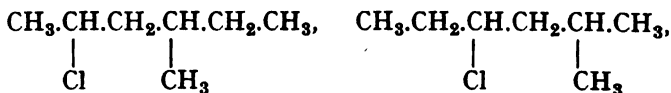
In the succeeding members, the possibility of isomerism commences. There are two butanes ; similarly are there two chloropropanes :



We may thus regard the halogen atom in the same light as we regard a methyl group which replaces one of the hydrogen atoms in a hydrocarbon. But in addition to this, the halogen atom introduces one new possibility of isomerism. A hydrocarbon of the paraffin series consists entirely of methyl groups, hydrogen atoms of some of which are substituted by other methyl groups. A chlorohydrocarbon is similar, except that the *position* of the chlorine atom leads to isomerism in cases where the position of the methyl group allows of none. An example will make this clear. The two formulæ :



convey exactly the same idea ; the properties of the compounds of which these formulæ are the ideographs are absolutely identical. On the other hand, if we replace one of the substituting methyl groups by a chlorine atom :



it will be seen that the two formulæ, when read from the left and from the right, are not identical. In one of the compounds

the chlorine atom is attached to the penultimate carbon atom, in the other to the antepenultimate. It need hardly be stated that in those cases where the formulæ are alike only one such compound exists, and that where they differ, more than one compound has been shown to exist. Our system of chemical shorthand writing must invariably be in harmony with the observed facts.

From a practical point of view the importance attaching to the halogenated derivatives of hydrocarbons is considerable, as, owing to the ease with which the halogen atom is replaced, they form invaluable materials for the synthesis of more complex organic compounds. Apart from this faculty they present but few points of interest, as they resemble one another very closely in chemical properties.

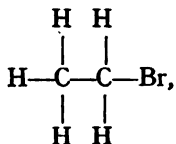
There is, however, one aspect which cannot too strongly be emphasised—the difference in chemical character of metallic halides (or hydrogen halides) and halogen-substituted hydrocarbons.

Hydrochloric acid and its salts, as is well known, are dissociated in solution, yielding chlorine ions :



On treatment with silver nitrate in either aqueous or alcoholic solution, an immediate precipitate of silver chloride is produced. Dissociation of metallic and similar chlorides is also indicated by the fact that such solutions are good conductors of electricity.

Chlorine-substitution-products of hydrocarbons, on the other hand, are insoluble in water, and neither conduct an electric current in alcoholic solution, nor yield immediate precipitates of silver chloride with silver nitrate. We therefore regard them as not ionisable, and this conception must be read into all formulæ, such as :



and added to the number of facts already implied by these ideographs. Further it must be borne in mind that the double decompositions, which are to be described below in connection with organic halogen compounds are not to be regarded as in any way resembling the practically instantaneous ionic reactions of inorganic chemistry, but as slower changes which take place with a definite, and in many cases measurable, velocity.

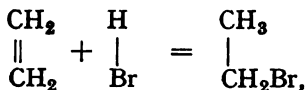
MONOHALOGENATED DERIVATIVES OF SATURATED HYDROCARBONS

As above indicated, the three general methods of formation are substitution, addition, and esterification. The first two of these find no great practical application in the preparation of monohalogenated derivatives of saturated hydrocarbons—or, as they are more generally termed, *alkyl halides*—but the third method is of wide application, and can be brought about in various ways.

(1) The feature which renders substitution impracticable as a mode of preparation, is the difficulty with which the course of the reaction can be controlled. Thus if chlorine be allowed to interact with methane in diffused daylight, we obtain a mixture containing monochloromethane CH_3Cl (methyl chloride) dichloromethane CH_2Cl_2 (methylene chloride), trichloromethane CHCl_3 (chloroform), and tetrachloromethane CCl_4 (carbon tetrachloride), as well as unchanged methane and hydrogen chloride. Owing to the proximity of their boiling-points, these compounds can be separated only by a tedious process of fractional distillation.

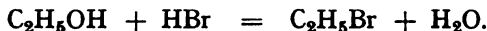
Compounds of chlorine and bromine only can thus be prepared; iodine does not react with saturated hydrocarbons.

(2) The addition of hydrogen halides to ethylenic compounds leads to the formation of monohalogenated compounds:

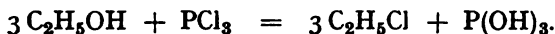


but since the ethylenic hydrocarbons necessary for the production of alkyl halides by this method are not readily procurable, this method is of limited applicability.

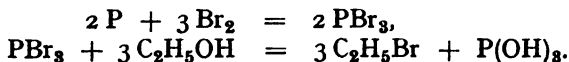
(3) The conversion of alcohols into the corresponding esters of halogen hydracids constitutes the chief method of preparing alkyl halides. This may be done simply by heating the alcohol with a saturated aqueous solution of the hydrogen halide :



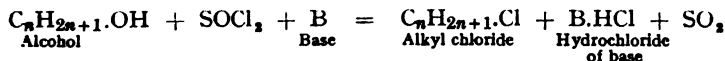
It is often more convenient to employ a phosphorus halide :



When preparing alkyl bromides or iodides, it is unnecessary to make use of phosphorus tribromide or phosphorus triiodide as such. If red phosphorus be suspended in the alcohol, and the requisite quantity of bromine or iodine added, the phosphorus halide is produced, which at the moment of formation, reacts with the alcohol :



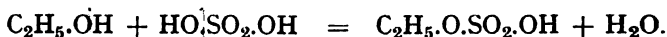
In addition to halides of phosphorus, other inorganic halides may be employed. For instance, alcohols can be converted into the corresponding chlorides by treatment with thionyl chloride SOCl_2 in presence of a suitable organic base, which absorbs free acid :



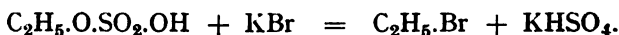
(where B represents a molecule of the organic base).

Finally, an alkyl halide may be obtained by heating a solution of concentrated sulphuric acid in the corresponding alcohol with a metallic halide. Thus on distilling a mixture of ethyl alcohol, sulphuric acid, and potassium bromide, ethyl bromide is produced. The reaction is somewhat more complicated than those hitherto described; *e.g.*: ethyl alcohol and the sulphuric acid first react together, forming ethylsulphuric acid (see p. 196), an ester which may be regarded as

sulphuric acid in which one of the hydrogen atoms is replaced by an ethyl group :



This ethylsulphuric acid then reacts with potassium bromide, whereby the sulphuric acid radicle is replaced by a bromine atom:

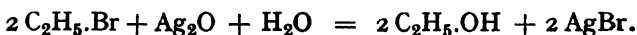


The reactions of alkyl halides are set forth in the following summary, taking ethyl bromide as a typical member :

(a) On boiling with dilute aqueous alkalies or alkali carbonates the alcohols are formed. This is merely the hydrolysis of an ester of a halogen hydracid :



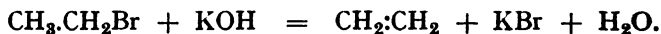
The same effect is produced on shaking with moist silver oxide :



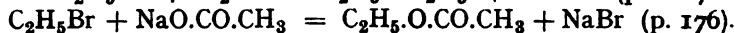
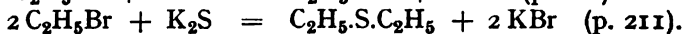
(b) On boiling with alcoholic potash two reactions take place; firstly the formation of the ethyl ether :



secondly the elimination of hydrogen halide, yielding the ethylenic hydrocarbon :



(c) With some salts of alkali metals, an alkyl radicle replaces the metallic atom :

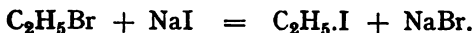


(d) With ammonia, addition takes place :



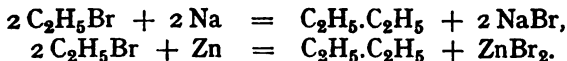
with replacement of the halogen atom by a nitrogen atom.

(e) Alkyl iodides can be prepared from alkyl chlorides or bromides by boiling with a solution of sodium or potassium iodide in alcohol or acetone :

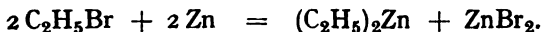


The metallic chloride or bromide, being insoluble in alcohol or acetone, is precipitated from solution.

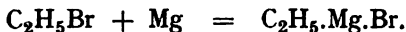
(f) Alkyl halides react with some of the more electro-positive metals, such as potassium, sodium, zinc, or magnesium, with elimination of metallic halide and production of hydrocarbons containing twice the number of carbon atoms as the original alkyl group :



When, however, an excess of zinc or magnesium is employed, *organo-metallic* compounds are formed. Thus two equivalents of ethyl bromide, on treatment with four equivalents of zinc, yield *zinc diethyl* :



With magnesium, acting on dry ethereal solutions of alkyl halides, *organo-magnesium halides* (Grignard's reagents) are produced :



These organic derivatives of metals are highly reactive. A summary of their properties will be found on pages 235-237.

INDIVIDUAL ALKYL HALIDES

The following table shows the boiling-points of some of the lower members of the series :

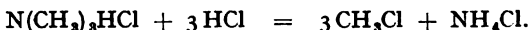
		Chloride.	Bromide.	Iodide.
Methyl	CH_3-	-24°	4°	45°
Ethyl	$\text{CH}_3.\text{CH}_2-$	12°	38°	72°
n. Propyl	$\text{CH}_3.\text{CH}_2.\text{CH}_2-$	46°	71°	102°
Isopropyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{CH}- \end{array}$	36°	60°	89°

H

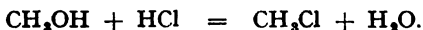
It will be seen that the boiling-points of the chlorides lie approximately 25° below those of the corresponding bromides, which in turn lie about 30° below those of the iodides.

Methyl chloride, methyl bromide, and ethyl chloride are gases under ordinary atmospheric conditions, the remaining members being all liquids. The chlorides have all specific gravity less than unity; the bromides and iodides are all heavier than water. Alkyl halides are insoluble in water, but miscible with organic liquids.

Methyl chloride CH_3Cl , a colourless gas, is prepared in large quantities as a by-product in the sugar refining industry (see p. 282) by heating the trimethylamine $\text{N}(\text{CH}_3)_3$ (p. 204), which occurs in beet residues, in a current of hydrogen chloride:



It is also manufactured on a large scale by the interaction of hydrogen chloride and methyl alcohol:



It is liquefied by compression, and is employed for the production of cold; also in surgery as a local anæsthetic.

Methyl bromide CH_3Br finds no great application either in technical practice or in the laboratory.

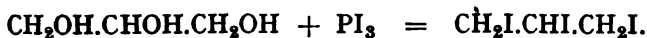
Methyl iodide CH_3I is largely employed as a "methylating" agent, that is, as a reagent by means of which hydrogen or metallic atoms in certain organic compounds can be replaced by methyl (CH_3 —) radicles. It is a colourless, very volatile oil, which is considerably heavier than water.

Ethyl chloride $\text{CH}_3\text{CH}_2\text{Cl}$ is a colourless mobile liquid, which can be stored at ordinary temperatures only under slight pressure, as it boils at 12° . It is employed technically in the manufacture of certain drugs, such as "sulphonol" (p. 214), and, like methyl chloride, finds in surgery a limited application as a local anæsthetic. It is prepared by the action of hydrogen chloride upon a mixture of zinc chloride and ethyl alcohol.

Ethyl bromide $\text{CH}_3\text{CH}_2\text{Br}$, a heavy, colourless, very volatile liquid, may be prepared either by the interaction of ethyl alcohol, sulphuric acid, and potassium bromide (p. 95) or by the gradual addition of bromine to a suspension of red phosphorus in ethyl alcohol. It is occasionally employed as an "ethylating" agent.

Ethyl iodide $\text{CH}_3\text{CH}_2\text{I}$ closely resembles methyl iodide, and may be prepared in exactly the same manner, by the interaction of ethyl alcohol, red phosphorus, and iodine. It is employed rather more generally than ethyl bromide for ethylation.

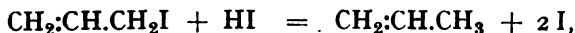
Of the remaining alkyl halides, the only one of especial interest is **isopropyl iodide** $\text{CH}_3\text{CHI.CH}_3$. This is produced by the action of red phosphorus and iodine upon a mixture of glycerol $\text{CH}_2\text{OH.CHOH.CH}_2\text{OH}$ (p. 130) and water. It is assumed that a normal reaction at first takes place, with formation of α,β,γ -tri-iodopropane :



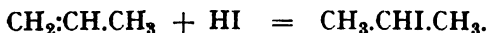
This loses two atoms of iodine, yielding allyl iodide (see below):



The water reacts with the phosphorus iodide, yielding hydrogen iodide ; this reacts with allyl iodide, yielding propylene :



which at once reacts with more hydrogen iodide, yielding isopropyl iodide :



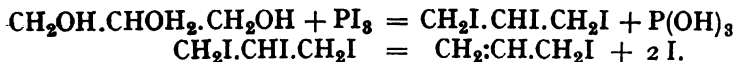
MONOHALOGEN-SUBSTITUTED DERIVATIVES OF UNSATURATED HYDROCARBONS

The most important members of this series are the **allyl** derivatives :



These are prepared from glycerol, through allyl alcohol (p. 126).

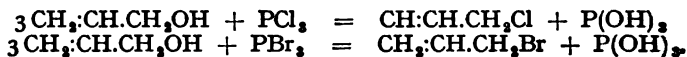
Allyl iodide may be directly prepared by the interaction of phosphorus and iodine with *dry* glycerol :



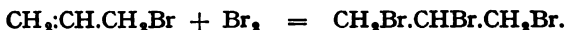
The absence of water is imperative, otherwise hydrogen iodide is produced, which would lead to the formation of isopropyl iodide. Allyl iodide boils at 103° .

Allyl chloride and **allyl bromide**—colourless liquids of characteristic odour, boiling at 46° and 70° respectively—may be prepared

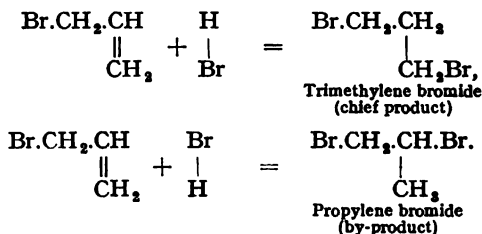
by the action of phosphorous chloride or bromide upon allyl alcohol :



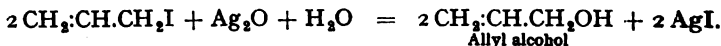
They readily yield addition-products with halogens ; thus allyl bromide at once takes up bromine, with formation of $\alpha.\beta.\gamma$ -tribromopropane (" tribromohydrin ") :



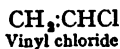
With hydrogen halides they yield trimethylene halides, together with traces of propylene halides :



Otherwise, in chemical character, the allyl halides closely resemble the saturated alkyl halides ; they may, for instance, be converted into allyl alcohol by the action of moist silver oxide :



Mono-halogen derivatives of ethylenic hydrocarbons also exist, in which the halogen atom is situated on a carbon atom to which the double bond is attached. The simplest examples of these are the **vinyl** halides :

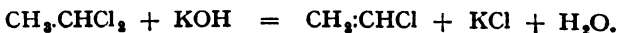


These are also termed *monochloroethylene*, *monobromoethylene*, and *monoiodoethylene*, these names clearly expressing their constitution as halogenated ethylenes.

They are produced by the action of solid alkalies upon ethylene dihalides (p. 104) :



or upon ethylidene halides (p. 103) :



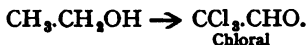
POLYHALOGEN-SUBSTITUTED DERIVATIVES OF HYDROCARBONS

We have seen that by the action of chlorine on methane a mixture of chlorine-substituted derivatives of methane is formed. These substances are :

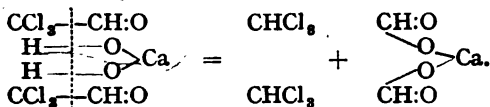
Methyl chloride	CH_3Cl	Gas
Methylene chloride	CH_2Cl_2	B.P. 41°
Chloroform	CHCl_3	B.P. 61°
Carbon tetrachloride	CCl_4	B.P. 76°

The most important of these is **chloroform**, CHCl_3 . This is prepared by the action of bleaching powder $[\text{CaCl}(\text{OCl})]$ in aqueous solution upon ethyl alcohol or acetone.

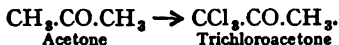
In the case of ethyl alcohol, the reaction follows some course such as the following : the bleaching solution acts simultaneously as an oxidising and chlorinating agent, converting the alcohol into chloral, or trichloroacetaldehyde (p. 151) :



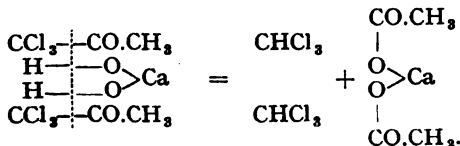
Chloral is unstable in presence of alkalis, and breaks down, by the action of the free lime present in the bleaching powder, into chloroform and calcium formate :



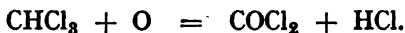
In the case of acetone, trichloroacetone is at first formed :



This breaks down in a similar manner by the action of calcium hydroxide, yielding chloroform and calcium acetate :



Chloroform is largely employed in surgery as an anæsthetic. One of the dangers attending its use depends upon the fact that atmospheric oxygen, under the influence of daylight, decomposes chloroform with formation of carbonyl chloride ("phosgene") COCl_2 , a violent poison :

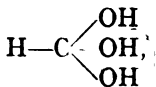


This decomposition is to some extent retarded by the admixture of a small proportion of alcohol. As an additional precaution, chloroform for anæsthesia should always be stored in bottles of dark glass which are filled as completely as possible.

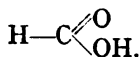
Chloroform derives its name from the fact that on prolonged heating with aqueous alkalis it yields sodium formate :



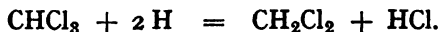
Its relation to formic acid can be seen if we regard it as the chloride of the hypothetical trihydroxylic alcohol



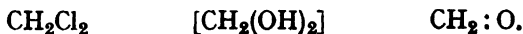
which would be the hydrate of formic acid



On treatment with zinc and hydrochloric acid in alcoholic solution, chloroform is reduced to **methylene chloride** CH_2Cl_2 :

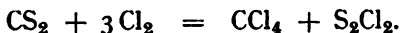


The relation of this substance to formaldehyde is shown by the action of moist silver oxide, which converts it into formaldehyde. Methylene chloride may thus be regarded as the hydrochloric ester of the dihydroxylic alcohol $\text{CH}_2(\text{OH})_2$, which is the hydrated form of formaldehyde $\text{CH}_2\text{:O}$:

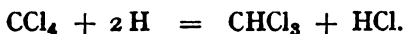


The final product of chlorination of methane, **tetrachloromethane** or **carbon tetrachloride** CCl_4 , is generally prepared

by the action of chlorine on carbon disulphide CS_2 , sulphur chloride S_2Cl_2 being formed as a by-product :

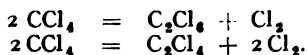


Carbon tetrachloride is largely employed as a solvent for bromine or iodine, as well as for fats, oils, and other technical products. It can be reduced by zinc and sulphuric acid to chloroform :



This reduction may be continued, by the use of sodium amalgam, until methane itself is produced.

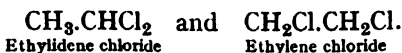
On passing the vapour of carbon tetrachloride through a heated tube, chlorine is liberated, with formation of hexachloroethane C_2Cl_6 , which is accompanied by small quantities of tetrachloroethylene C_2Cl_4 :



Of the analogous compounds of bromine and iodine the most important is **iodoform** CHI_3 . This is a yellow crystalline solid melting at 119° , formed by the action of iodine on an alkaline aqueous solution of alcohol or acetone, its mode of formation following the same lines as that of chloroform (p. 101). It is largely employed in surgery as an antiseptic. On reduction it yields methylene iodide CH_2I_2 .

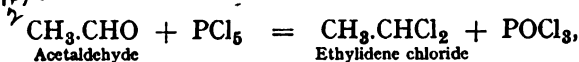
Carbon tetrabromide CBr_4 , a white solid melting at 94° , is produced by the action of alkali hypobromite solutions upon a large number of organic compounds, especially sugars, starches, and cellulose.

Turning now to the polyhalogen derivatives of hydrocarbons containing more than one atom of carbon, we may first consider the dichloroethanes. As was stated in a previous chapter (p. 10), two dichloroethanes $\text{C}_2\text{H}_4\text{Cl}_2$ can exist, the constitutions of which are expressed by the formulæ :



The first of these, **ethylidene chloride**, is produced by

the action of phosphorus pentachloride upon acetaldehyde (p. 146) :



and on hydrolysis yields again acetaldehyde. Bearing in mind that the constitution of aldehyde is $\text{CH}_3\text{CH:O}$, we conclude from these facts that the two chlorine atoms are attached to one and the same carbon atom. Ethylidene chloride is a colourless liquid, which boils at 58° .

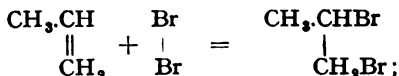
The other dichloroethane, **ethylene chloride** (or **ethylene dichloride**), is produced by the combination of ethylene and chlorine. The fact that on hydrolysis it yields an alcohol (ethylene glycol, p. 127) which can be shown to contain two exactly similar hydroxyl groups, leads us to regard the two chlorine atoms as being attached to different carbon atoms, one to each. For were this not so, then this dihydroxylic alcohol would have to contain the two hydroxyl groups attached to the same carbon atom—a grouping which is known to be unstable and would readily allow of dehydration to an aldehyde.

Ethylene chloride is a colourless liquid boiling at 83° ; **ethylene bromide** $\text{CH}_2\text{Br.CH}_2\text{Br}$, melts at 8° and boils at 171° , and finds wide application in organic synthesis. **Ethylene iodide** is a solid, melting at 71° .

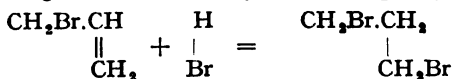
Similar to ethylene bromide are **propylene bromide** :



prepared by passing propylene (p. 85) into bromine :

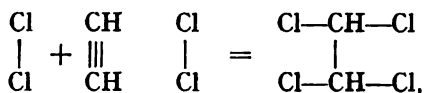


and **trimethylene bromide** $\text{CH}_2\text{Br.CH}_2\text{CH}_2\text{Br}$, prepared by the addition of hydrogen bromide to allyl bromide (p. 99) :

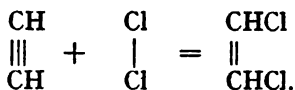


Some of the more highly chlorinated derivatives of ethane find application as solvents, for example for the cleansing of clothes. Such are trichloroethane, tetrachloroethane, and

pentachloroethane. It will be noted that there are two possible trichloroethanes: one in which the chlorine atoms are all attached to one carbon atom, $\text{CH}_3.\text{CCl}_3$, and one in which two chlorine atoms are attached to one carbon atom and one to the other, $\text{CH}_2\text{Cl}.\text{CHCl}_2$. Similarly there are two possible structures for tetrachloroethane: $\text{CH}_2\text{Cl}.\text{CCl}_3$ and $\text{CHCl}_2.\text{CHCl}_2$. Substances corresponding to both of these are known; the second is produced by the addition of chlorine to acetylene:



and is often called "acetylene tetrachloride." An "acetylene dichloride" is also formed as a first stage of the addition process:



This is the symmetrical dichloroethylene.

CHAPTER VII

ALCOHOLS

SATURATED MONOHYDROXYLIC ALCOHOLS

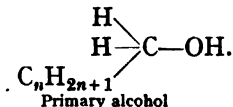
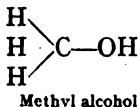
ALCOHOLS may be regarded as derivatives of water in which one of the hydrogen atoms is replaced by an organic complex. The justness of this view will be rendered amply clear by consideration of the modes of formation and reactions of alcohols.

Their composition may be expressed by the general formula $C_nH_{2n+2}O$, but as it has been established that all alcohols possess a hydroxyl group ($-OH$), we may rearrange this to $C_nH_{2n+1}.OH$, in which the generic formulation of an alkyl group ($C_nH_{2n+1}.)$ is clearly shown.

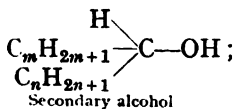
As in the case of the corresponding alkyl halides, isomerism is even more manifold than among the paraffin hydrocarbons, since the position of the hydroxyl group in the chain introduces a new factor of difference.

We may subdivide saturated aliphatic alcohols into three great classes: designated *primary*, *secondary*, and *tertiary*.

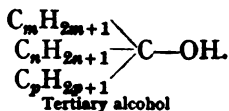
Primary alcohols are those in which at least two hydrogen atoms are attached to the carbon atom to which the hydroxyl group is attached:



Secondary alcohols contain two alkyl radicles and one hydrogen atom attached to this carbon atom:



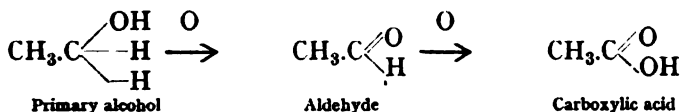
whilst in **tertiary alcohols** all the hydrogen atoms in this position are replaced by alkyl groups :



We may also regard the three types of alcohols as being distinguished by the three different groupings :



The chief point of difference between primary, secondary and tertiary alcohols is their behaviour on oxidation. Primary alcohols yield firstly aldehydes and then acids, the number of carbon atoms in the molecule of the products remaining the same as in the original alcohol, *e.g.* :

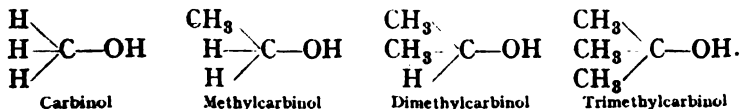


Secondary alcohols yield ketones, which on further oxidation break down into acids containing a less number of carbon atoms, *e.g.* :



Tertiary alcohols are broken down on oxidation, yielding products containing fewer carbon atoms in the molecule,

A convenient system of nomenclature of alcohols is the following. Starting with methyl alcohol under the name "carbinol," all alcohols may be designated as substitution products of carbinol, and by the name it can be at once designated whether the alcohol referred to is primary, secondary or tertiary. To take as examples the methyl derivatives, we have :



GENERAL PHYSICAL AND CHEMICAL PROPERTIES OF ALCOHOLS

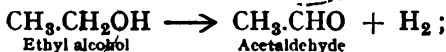
We have seen (p. 32) that alcohols react with acids, forming esters, just as metallic oxides yield salts. But the nature of alcohols and esters is very different from the nature of bases and salts. Whilst in bases the hydroxyl group is ionised in aqueous solution, yielding alkaline solutions, alcohols are neutral bodies and show no sign of electrolytic dissociation in solution. Similarly, on dissolving in water, salts yield ions of their acidic radicle and metal, while esters do not possess this property. The alcoholic hydroxyl group is thus entirely distinct in its chemical behaviour from the hydroxyl group in metallic hydroxides.

The lowest members of the series (C_1 to C_3), are colourless, mobile liquids, neutral to litmus, and miscible in all proportions with water, from which mixture they can be separated by the ample addition of solid potassium carbonate. They possess pleasant odours and burning taste, and burn in air with a smokeless flame of slight luminescence.

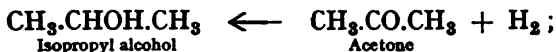
The members containing five to ten carbon atoms are colourless, oily liquids, the solubility of which in water decreases on ascending the series. Their odour is in some cases distinctly unpleasant. They burn in air with a luminous and often smoky flame.

The higher members, containing twelve or more atoms of carbon in the molecule, are in general waxy solids, insoluble in water, and without pronounced odour. Those containing sixteen carbon atoms and more can be distilled without decomposition only under reduced pressure.

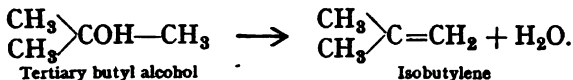
The principal general reactions of alcohols have been discussed on pages 29–34. Of importance is the following method of distinguishing between primary, secondary and tertiary alcohols:—on passing the vapour of the alcohol over finely-divided metallic copper maintained at a temperature of about 300° , primary alcohols decompose into aldehydes and hydrogen:



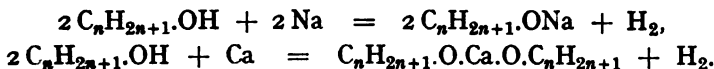
secondary alcohols decompose into ketones and hydrogen :



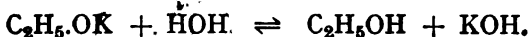
whilst tertiary alcohols are dehydrated under these conditions, yielding ethylenic hydrocarbons and water ;



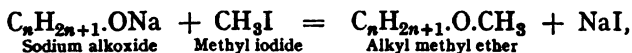
As has already been stated (p. 34), alcohols, in addition to forming esters with acids of all sorts, also show their relationship to water in that they are capable of yielding metallic salts when treated with many of the more electropositive metals :



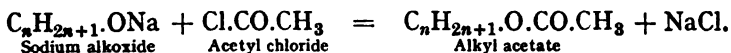
Metallic alkoxides are decomposed by water, with regeneration of the alcohol and metallic hydroxide. This reaction is a reversible one ; an equilibrium mixture is produced, the composition of which varies with the relative amounts of water and alcohol present, so that an alcoholic solution of an alkali hydroxide can react as a solution of an alkoxide :



They react with alkyl halides, with formation of ethers :



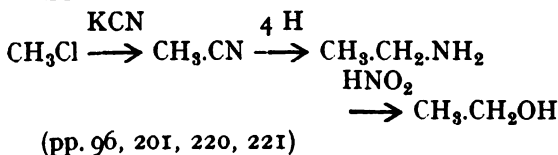
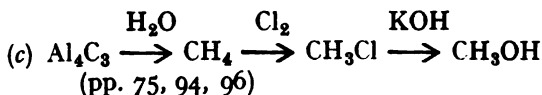
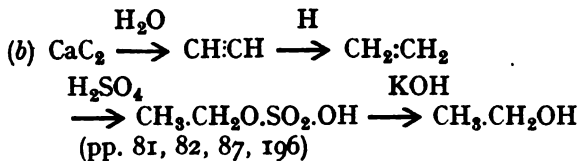
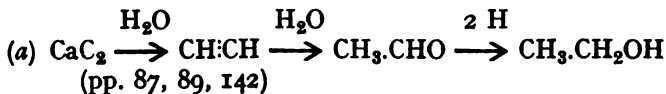
and with acid halides (p. 169) yielding esters (p. 174) :



The vapours of alcohols are stable up to a temperature of about 300° ; on heating more strongly, they are decomposed into saturated hydrocarbons, hydrogen, carbon monoxide, and other products.

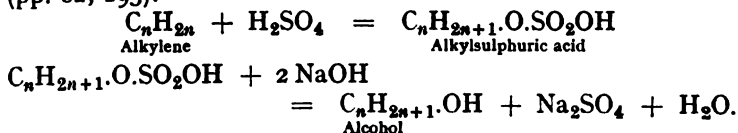
MODES OF FORMATION OF ALCOHOLS

From the elements.—The following schemes show some of the possible methods of producing alcohols from the elements :

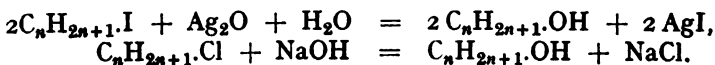


From organic compounds.—General methods for preparing primary, secondary, and tertiary alcohols are :

(1) From hydrocarbons of the ethylene series, by treatment with concentrated sulphuric acid, and subsequent hydrolysis (pp. 82, 193).

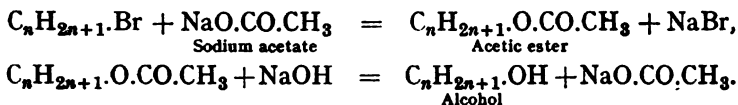


(2) From alkyl halides, by treatment with moist silver oxide or dilute alkalis or alkali carbonates :

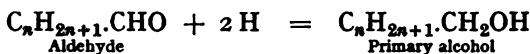


This reaction often furnishes better yields when an ester is produced as intermediate product, and then hydrolysed.

Either the silver or an alkali metal salt of a carboxylic acid may be employed :

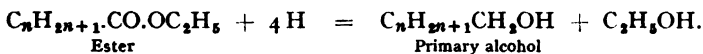


Formation of primary alcohols.—(1) Reduction of aldehydes and acids. Aldehydes are more suitable for this purpose, inasmuch as they are more readily reduced :

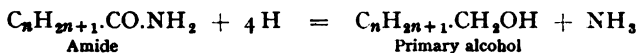


The reduction may be effected either by treatment with sodium amalgam in water, or, in the case of aldehydes insoluble in water, zinc dust in glacial acetic acid may be employed. An excellent method for the reduction of fairly volatile aldehydes is to pass a mixture of aldehyde vapour and hydrogen over finely-divided nickel at about 150°.

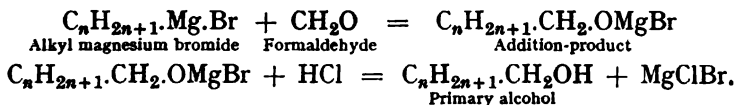
Although free carboxylic acids themselves are reduced with difficulty, certain of their derivatives are more amenable to the influence of reducing agents. Thus primary alcohols can be obtained by the action of metallic sodium upon a solution of an ester in absolute alcohol :



Amides and acid anhydrides can also be forced to yield primary alcohols :



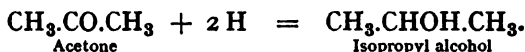
(2) By the action of alkyl magnesium halides (p. 236) upon formaldehyde,¹ and subsequent treatment of the addition-product with dilute acid :



Formation of secondary alcohols.—(1) Reduction of ketones.

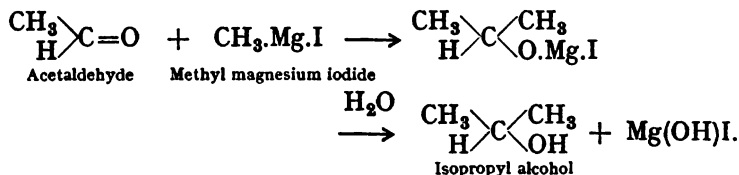
¹ The polymeric "polyoxymethylene" (CH₂O)_n (p. 147) is generally employed in place of formaldehyde.

This may be best effected, when the ketone in question is sufficiently volatile, by passing a mixture of the vapour of the ketone with hydrogen over heated nickel :

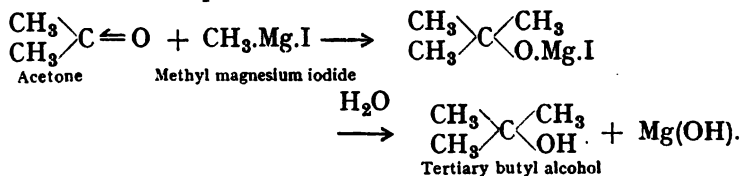


Sodium amalgam in presence of water may also be employed.

(2) Secondary alcohols are formed by the action of alkyl magnesium halides upon aldehydes other than formaldehyde. The reaction follows the same course :



Formation of tertiary alcohols.—By the action of alkyl magnesium halides upon ketones :



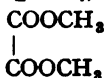
INDIVIDUAL MONOHYDROXYLIC ALCOHOLS

<i>Alcohol.</i>		<i>Boiling-point.¹</i>
Methyl	CH ₃ OH	64°
Ethyl	CH ₃ .CH ₂ OH	78°
<i>n</i> -Propyl	CH ₃ .CH ₂ .CH ₂ OH	97°
Isopropyl	CH ₃ .CHOH.CH ₃	81°
<i>n</i> -Butyl	CH ₃ .CH ₂ .CH ₂ .CH ₂ OH	117°
Isobutyl	(CH ₃) ₂ CH.CH ₂ OH	107°
Tertiary Butyl	(CH ₃) ₃ COH	83°
<i>n</i> -Amyl	CH ₃ .CH ₂ .CH ₂ .CH ₂ .CH ₂ OH	138°
Isoamyl	(CH ₃) ₂ CH.CH ₂ .CH ₂ OH	130°
Active Amyl	CH ₃ .CH ₂ .CH(CH ₃).CH ₂ OH	128°

¹ This list of boiling-points is intended merely to demonstrate the rise of boiling-point accompanying the increase in the number of carbon

Methyl alcohol CH_3OH is a colourless liquid of faintly spirituous odour, miscible in all proportions with water. It burns in air with a bluish smokeless flame of slight luminescence. It acts poisonously on the human system when taken in quantity. At low temperatures it solidifies to colourless crystals melting at about -94° .

Methyl alcohol occurs as a constituent of the products of the destructive distillation of wood, which is heated in iron retorts at as low a temperature as practicable. The watery distillate, known as "wood vinegar," contains from 1 per cent. to 2 per cent. of methyl alcohol, 0.17 to 0.5 per cent. of acetone, and about 10 per cent. of acetic acid. This is then distilled, and the vapour passed through a suspension of slaked lime, by which the acetic acid and other acid constituents are removed. The distillate containing neutral and alkaline substances is freed from insoluble oils by mixing with water, and the mixture fractionally distilled over lime, which has the effect of hydrolysing any methyl acetate present. The crude "wood spirit" thus obtained is then boiled with anhydrous oxalic acid (p. 184); on cooling, methyl oxalate



crystallises out. This is separated and boiled with water or ammonia, whereby it is hydrolysed with liberation of pure methyl alcohol, which is again collected by fractional distillation, and finally rectified after drying over quicklime.

The crude wood spirit, from which the acetic acid has been removed, is employed for the denaturation of ethyl alcohol in the manufacture of methylated spirit, as will be referred to below.

In its chemical reactions methyl alcohol is a typical primary alcohol, but it differs from the subsequent members by the fact that dehydration leads to the formation not of ethylene hydrocarbons, but methyl ether, since there is no second carbon atom with which a double bond could be formed:



while on heating with concentrated sulphuric acid, methyl ether or methyl sulphate $\text{CH}_3\text{O.SO}_2\text{OCH}_3$ is produced, according to the conditions.

atoms in the molecule, and is in no wise to be regarded as an object for memorisation.

Ethyl alcohol $\text{CH}_3\text{CH}_2\text{OH}$ is a colourless mobile liquid of pleasant odour; miscible in all proportions with water. On making a mixture of ethyl alcohol and water, heat is developed, and the total volume of the mixture is less than the sum of those of its constituents. The maximum contraction takes place on mixing 52 volumes of the alcohol with 48 volumes of water; the resulting mixture occupies 96.3 volumes. It boils at 78° under ordinary atmospheric pressure and solidifies at about -112° . Its specific gravity at 0° is 0.806, referred to water at 0° .

Ethyl alcohol, which is the "alcohol" of daily parlance, is produced by the fermentation of sugars, in particular glucose (p. 275) by means of yeast, carbonic acid being simultaneously formed:



Little is known of the mechanism of this reaction.

Yeast consists of a collection of minute living organisms, which nourish themselves upon the sugar solution, and eliminate ethyl alcohol and carbon dioxide as excreta. The presence, however, of living organisms is not necessary, for it has been found that on macerating yeast with a little water, and filtering the mixture under great pressure so as to produce a clear homogeneous solution, this filtrate can also bring about the conversion of glucose into ethyl alcohol and carbon dioxide. The filtered solution contains a substance called an *enzyme*, known as *zymase*, which can bring about the change without the intervention of organised life. It is hence termed an *unorganised ferment*; yeast, which is a collection of living cells which rapidly multiply in the nutrient liquid, is termed an *organised ferment*, and may be regarded as a colony of organisms, capable of digesting glucose by means of the enzyme contained in their alimentary system. In this the yeast organism is not without parallel; in all animals digestion is carried out by the aid of enzymes which are secreted in the alimentary canal.

A minute quantity of an enzyme is capable of effecting an indefinite amount of chemical reaction. The rate at which

enzymes bring about chemical changes is to a great extent dependent on the temperature. As a rule they work most rapidly at about 40°C . ; below 40° the rate of reaction decreases with fall of temperature ; if heated much above 40° they are "killed," or rendered inactive.

Many of the enzymes besides zymase are now known, each of which is capable of accelerating the speed of some one reaction to many thousand times its velocity under ordinary conditions.

In the fermentation process, besides ethyl alcohol, smaller quantities of higher alcohols—propyl, butyl, isobutyl, isoamyl, etc.—are formed. These are presumably produced not from the sugar itself, but from proteins (p. 293) associated with the yeast. The mixture of higher alcohols, of which isoamyl alcohol is the principal constituent, is known as "fusel oil." ("Fusel" is the German name for a cheap spirit, rich in these higher alcohols, produced by the fermentation of potatoes.) The ethyl alcohol is isolated from the fermented mixture by means of fractional distillation. In this way a spirit of about 90 per cent. strength is obtained.

The very strongest spirit obtainable by fractionation contains 4.43 per cent. of water, for ethyl alcohol forms with water a constant-boiling binary mixture, containing 95.57 per cent. of alcohol, and boiling at 78.15° —lower than pure alcohol, which boils at 78.30° . To prepare absolute alcohol, therefore, the 95 per cent. spirit must be dried by treatment with quicklime before its final distillation.

Absolute alcohol rapidly absorbs moisture from the air. Traces of water can be detected by treatment with anhydrous copper sulphate, which acquires a blue tint in presence of moisture ; or with calcium carbide, which evolves acetylene on contact with moisture, but does not react with alcohol.

The strength of a sample of aqueous alcohol is generally estimated, when the concentration of alcohol exceeds 10 per cent., by determining the density with a hydrometer. When the sample contains less alcohol, a definite amount is distilled over and the density of the distillate determined.

The principal qualitative test for ethyl alcohol is the

formation of iodoform (p. 103) on addition of alkali and iodine to its aqueous solution. This test is not given by methyl alcohol.

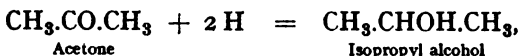
In the manufacture of alcohol, pure glucose, which is a relatively expensive commodity, is not employed. The sugar solution upon which the yeast is to act is prepared either by the treatment of crude starch (potatoes, grain, etc.) with malt, which contains a ferment called *diastase*, capable of converting starch into the sugar maltose (p. 280), or by the hydrolysis of cellulose by treatment with sulphuric acid (p. 285).

By far the greatest quantity of ethyl alcohol manufactured is employed for drink. Alcoholic beverages may be divided into two classes: those distilled and those not distilled. The latter class includes beers (by fermentation of malted grain liquor, containing from 3 per cent. to 6 per cent. of alcohol) and wines (by fermentation of grape juice, containing from 5 per cent. to 20 per cent. of alcohol); while the former comprises spirituous liquors such as brandy and cognac (by distillation of wines or wine residues, containing 30 per cent. to 50 per cent. of alcohol), rum (from fermented sugar cane liquors), arrack (from rice), etc.

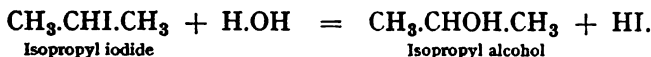
Methylated spirit consists of ethyl alcohol containing 5 per cent. to 10 per cent. of water and varying amounts of crude wood spirit (methyl alcohol, acetone, and other products) which latter ingredient is added with the intention of rendering the spirit unfit to drink. As this, however, has not universally led to the desired result, further denaturation by the addition of paraffin hydrocarbons and, in France, of pyridine (an organic base, p. 455), is occasionally effected. Methylated spirit is therefore only lightly taxed, as it serves as fuel for spirit lamps without encroaching on the domain of alcoholic beverages. The presence of paraffins in spirit can be detected by the formation of a turbidity on diluting a sample with water.

Normal propyl alcohol $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ closely resembles ethyl alcohol in general properties. It occurs in the higher-boiling fractions of the crude spirit obtained by distillation of the products of alcoholic fermentation of sugar. It cannot be completely separated from water by distillation, since, like ethyl alcohol, it forms with water a binary mixture boiling at a constant temperature below that of the pure alcohol.

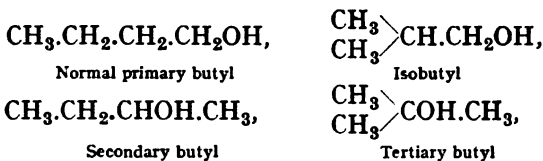
Isopropyl alcohol $\text{CH}_3.\text{CHOH}.\text{CH}_3$ is obtained by the reduction of acetone (p. 152):



or by the hydrolysis of isopropyl halides by boiling with water in presence of lead oxide:



Butyl alcohols, $\text{C}_4\text{H}_9\text{OH}$. Of the four isomeric alcohols of the composition $\text{C}_4\text{H}_9\text{OH}$:



the most important is the primary **isobutyl alcohol**. This substance occurs, together with ethyl, propyl, and amyl alcohols, among the products of alcoholic fermentation of sugar. Its constitution has been proved by the formation of *isobutyric acid* $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \rangle \text{CH}.\text{COOH}$ (p. 166) on oxidation.

Primary normal butyl alcohol does not occur in fusel oil, but is produced by the action of certain ferments or bacteria upon mannitol $\text{CH}_2\text{OH} . (\text{CHOH})_4 . \text{CH}_2\text{OH}$ (p. 134), trimethylene glycol $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2\text{OH}$ (p. 130), or glycerol $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$ (p. 130). On oxidation it yields *normal butyric acid*:

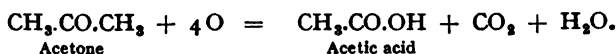
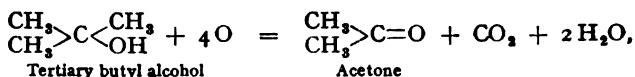


Secondary butyl alcohol can be prepared only by synthetic methods, such as reduction of methyl ethyl ketone:

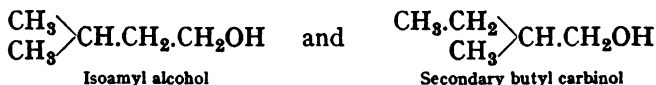


Tertiary butyl alcohol is a white crystalline solid melting at 25° and boiling at 83° . Its odour faintly resembles that of camphor—a characteristic common to many compounds containing three alkyl groups united to one carbon atom. On oxidation it

parts with one carbon atom, yielding acetone, which on further oxidation loses a second methyl group :



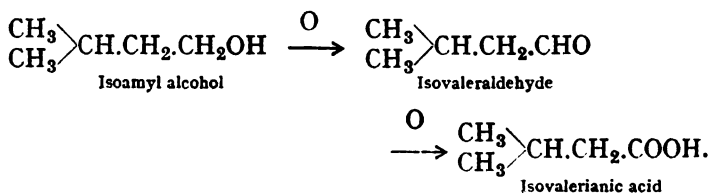
Amyl alcohols $\text{C}_5\text{H}_{11}\text{OH}$. Of the eight isomeric alcohols $\text{C}_5\text{H}_{11}\text{OH}$ only the two primary alcohols :



are of present interest. A mixture of these two isomers occurs in the products of alcoholic fermentation as the "amyl alcohol" boiling at $130\text{--}131^\circ$.

This mixture forms a nearly colourless liquid, only slightly soluble in water (at 20° a saturated solution contains about 3 per cent.), possessing a powerful and unpleasant odour. Its vapour frequently causes sick headaches when inhaled. The separation of the two alcohols, the properties of which are very similar, is a tedious and difficult process, involving the formation of a mixture of solid esters and the fractional crystallisation of these.

The principal constituent of the amyl alcohol obtained from fusel oil is **isoamyl alcohol** $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, which generally forms over 80 per cent. of the mixture. The "amyl alcohol" obtained from sugar residues contains about equal quantities of each of the two isomers. On oxidation it is converted to *isovalerianic* (isopropyl-acetic) acid *via* the corresponding aldehyde :



Secondary butyl carbinol $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \\ \text{CH}_3 \end{array} \text{CH} \cdot \text{CH}_2\text{OH}$ is a liquid closely resembling isoamyl alcohol. This constituent of fusel oil is of particular interest in that it is optically active, that is to say, it rotates the plane of polarised light. To make this property clear we must enter into the question of optical rotation.

Light is caused by transverse vibrations of particles of the ether—thus in a single ray of light the vibrations may take place in all directions in a plane perpendicular to the path along which the light is transmitted. Now certain minerals, such as tourmaline, are capable of transmitting light, but allow the passage of only those rays which vibrate in a definite plane—namely that perpendicular to the laminæ of the crystals. The transmitted light, the vibrations of which lie only in one plane, is termed “plane polarised.”

If light passing through such a plate of tourmaline be viewed through a second plate of tourmaline, it will be noticed that a maximum intensity of light is observed when the second

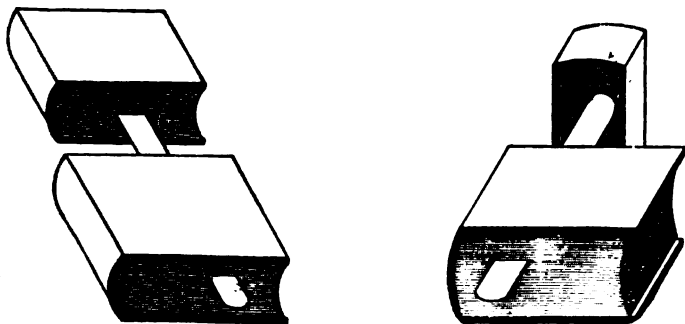


FIG. 7.

plate is held in a certain position, and that on rotating the plate through a right angle, the light is totally obstructed. The following comparison will serve to illustrate the condition of affairs. We may liken a ray of light to a lead-pencil, and the two plates of tourmaline to two closed books. The pencil

refuses to pass between the leaves of the first book, but readily does so as soon as it is cut down into a series of thin slivers resembling knife-blades. On laying both of the books flat on the table, the blades can be slipped between the leaves of both, but if the second book be placed upon its edge (having thus been turned through a right angle), the blades refuse to penetrate it, and not until it is again laid flat on the table can they lie between the leaves of both books.

Similarly, a maximum intensity of polarised light will pass through the second plate of tourmaline only when the laminae of the two crystals are in parallel positions.

Now it was discovered by Biot in 1815 that certain substances occurring in nature, such as turpentine, or solutions of such solids as sugar, camphor, or tartaric acid, rotate the plane of polarisation. That is to say, if a column of the liquid be placed between the two plates of tourmaline (constructed in the form known as Nicol's prisms), one of the Nicol's prisms must, in order to obtain a maximum transmission of light, be turned into a different position from that in which it was in the absence of the column of liquid.

Biot observed that these optically active substances rotate the plane of polarisation either in solution, in the form of vapour, or in an amorphous condition. On the other hand, it had been noticed in 1811 by Arago that crystals of quartz and certain other minerals were able to rotate the plane of polarisation. In these cases the optical activity is dependent upon the crystalline form, and is not a characteristic of the molecules, for a solution of such a crystalline substance is optically inactive. From these facts Biot concluded that this property of optically active organic bodies was a characteristic of the molecules themselves—not of aggregations of molecules.

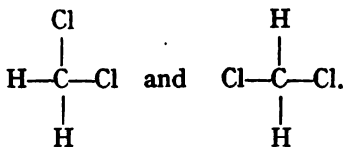
Rotation can take place in two senses:—*dextrorotatory* substances rotate to the right, or clockwise; *levorotatory* substances rotate to the left, or counter-clockwise. The angle of rotation is directly proportional to the length of column of liquid through which the polarised light passes; on doubling the length, the observed angle is doubled. It is customary to express the property as the *specific* rotation $[\alpha]$, calculated from the formula:

$$[\alpha]_D^t = \frac{\alpha}{l \cdot d},$$

where α represents the angle of rotation measured in the polarimeter; l the length, expressed in centimetres, of the column of liquid; and d the density, or weight in grams of one cubic centimetre of the liquid at the temperature t at which the observation is made. As the amount of rotation is dependent upon the wave-length of the transmitted rays, it is necessary to employ monochromatic light, the sodium D line being usually selected.

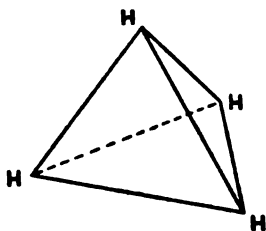
To return now to the question of the secondary butyl carbinol present in fusel oil, we have noted that it, like turpentine, rotates the plane of polarisation; the direction is counter-clockwise, or to the left. When pure, from whatever source, the degree of rotation of *laevo* amyl alcohol is always the same for equal lengths of liquids; the specific rotation $[\alpha]_D^{20^\circ}$ is -5.90° .

In the introductory chapter it was pointed out (p. 6) that in methane the four atoms of hydrogen were equivalent—that the same product was obtained on replacing any one of them by a different atom or group. Further, it was noted that methylene chloride (dichloromethane CH_2Cl_2) exists in only one form, although its formula can be written in two different ways:



To explain these facts, we must imagine some structure for methane in which all the hydrogen atoms stand in relatively the same positions to each other and to the carbon atom. This can be done only by assuming that the carbon atom is situated as at the centre of a sphere, on the periphery of which the hydrogen atoms are symmetrically grouped. They will then take up positions corresponding to the four corners of

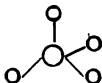
a regular tetrahedron, at the centre of which lies the carbon atom :



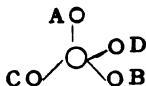
Their relative positions can also be indicated by placing four tennis balls together so that each touches the other three. The hydrogen atom can then be imagined as lying at the centre of each ball ; the carbon atom as reposing in the space between the four balls.

A moment's consideration will now make clear the explanation why only one dichloromethane exists.

It is immaterial how we depict this diagram ; what is important is that we should grasp the idea of the symmetrical distribution of the valencies in space. Perhaps the most simple plane formula to express this idea is the following :

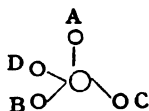
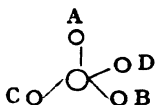


Let us now assume that we have four different atoms or groups attached to one and the same carbon atom. Designating these atoms or groups as A, B, C, and D, respectively, we obtain a diagram such as :



Now it is possible to arrange the four groups in two ways, so that by no amount of twisting and turning of the model can we render the two exactly identical ¹ :

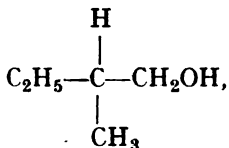
¹ The student is recommended to construct two such models out of corks and pins or matches. These will make the question clear to him in a way that is almost impossible with two-dimensional diagrams.



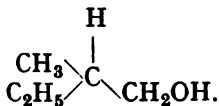
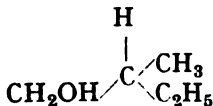
The two arrangements are, in fact, *mirror-images*; and as each of the members is different, these mirror-images¹ are *non-superposable*. This is, in principle, the outline of the famous theory developed independently by Van't Hoff and Le Bel.

Now it has been found that whenever an organic compound is capable of rotating the plane of polarised light, its structural formula can be written in two ways, such that the one is the *non-superposable mirror-image* of the other. And this is the case, among carbon compounds, only when four different atoms or groups are attached to one carbon atom. It has been found that for every compound which rotates the plane of polarisation there exists an isomeric compound, alike in every chemical respect, and alike in every physical property except that it rotates the plane to an equal degree in the opposite direction.

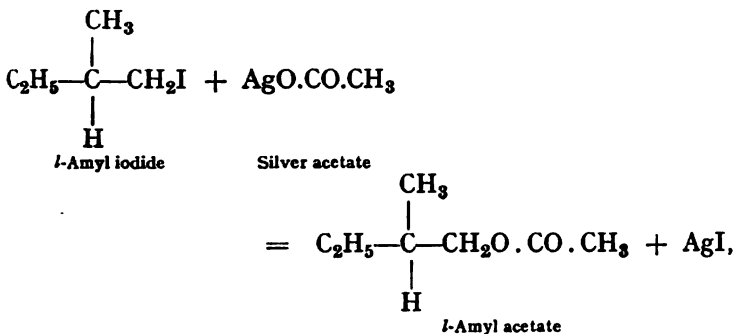
Let us now apply these statements to the optically active amyl alcohol of fusel: secondary butyl carbinol $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$. It is evident that here we have four different groups or atoms attached to one carbon atom:



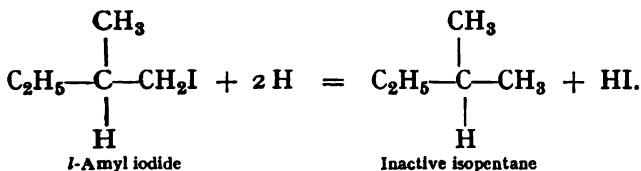
so that the formula can be arranged in two distinct three-dimensional structures which are non-superposable mirror-images:



¹ A similar case of two unsymmetrical objects which are mirror-images is before us every day: the human hands. The conception of the non-superposability of these mirror-images is brought out by the fact that right-hand and left-hand gloves are not interchangeable.



from which, on hydrolysis, the original active alcohol can be regenerated. On the other hand, if the active iodide be reduced by means of coppered zinc, a pentane is produced which is optically inactive, owing to the presence of two identical (in this case methyl) groups attached to the same carbon atom :



On examining a solid model, it will at once be evident that no two mirror-images can exist under these conditions ; the formulæ are always superposable :



The consideration of optically active compounds will again be taken up in a later chapter (p. 251).

UNSATURATED MONOHYDROXYLIC ALCOHOLS

Just as we have the saturated (paraffin) hydrocarbons $\text{C}_n\text{H}_{2n+2}$ and the ethylenic hydrocarbons (olefines) C_nH_{2n} , so

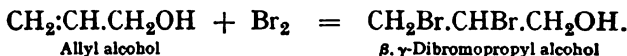
have we also a series of ethylenic alcohols $C_nH_{2n-1}OH$, which bear exactly the same relation to the saturated alcohols as do the olefines to the paraffins.

The best known ethylenic alcohol, and the only one which we need here consider, is **allyl alcohol**. This alcohol bears to normal propyl alcohol the same relation that propylene does to propane :

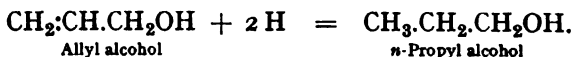


Allyl alcohol is prepared by heating oxalic acid (p. 184) with an excess of glycerol (p. 130). The mechanism of the reaction will be explained on p. 133.

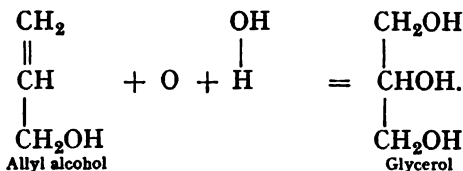
It is a colourless liquid of pungent odour, boiling at 96° . In chemical behaviour it resembles at once ethylene and ethyl alcohol. With bromide it immediately forms an addition-product, *β,γ -dibromopropyl alcohol* :



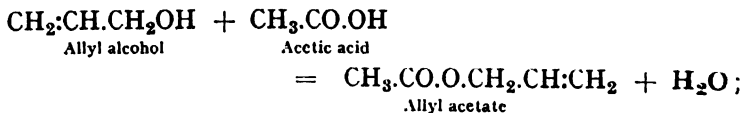
Similarly it combines with hydrogen chloride and hydrogen bromide, and may be reduced to normal propyl alcohol :



On gentle oxidation it is converted into glycerol :



It shows its alcoholic character by giving the usual reactions of an alcohol ; it can be esterified :



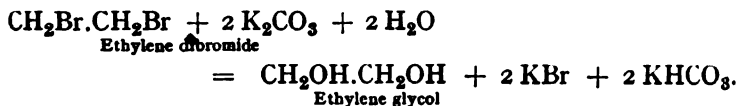
with phosphorus trichloride it yields allyl chloride (p. 99) ; and so on.

The corresponding alcohol in the acetylenic series is **propargyl alcohol** $\text{CH}_3\text{C}\cdot\text{CH}_2\text{OH}$. All that need be said of this compound is that it behaves both as an acetylenic compound (giving precipitates with ammoniacal silver and cuprous solutions) and as an alcohol.

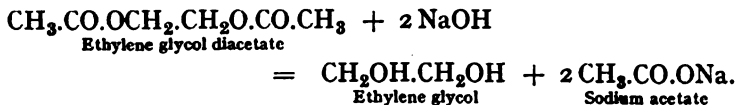
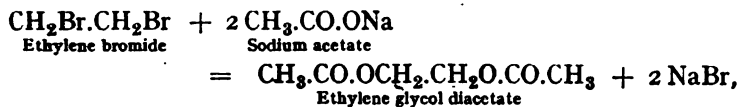
POLYHYDROXYLIC ALCOHOLS

DIHYDROXYLIC ALCOHOLS

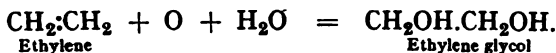
When ethylene is brought into contact with bromine, ethylene dibromide (α,β -dibromoethane) $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$ is formed (p. 104). From this dibromo compound we can obtain the corresponding dihydroxylic alcohol, by the same methods as those by which ethyl bromide is converted into ethyl alcohol. On prolonged boiling with dilute potassium carbonate solution ethylene dibromide yields **ethylene glycol** (or simply **glycol**) $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$:



It may also be prepared through the acetate :

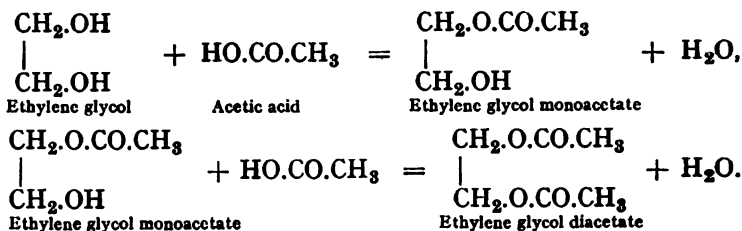


It can also be obtained by gentle oxidation of ethylene :

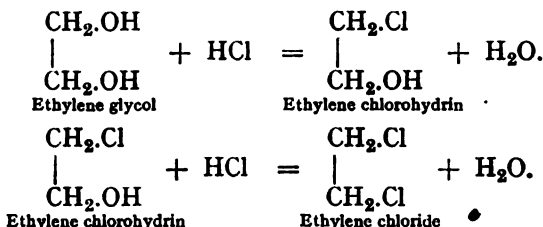


The term *glycol* is synonymous with " dihydroxylic alcohol " ; and, in accordance with this, glycols behave as true alcohols.

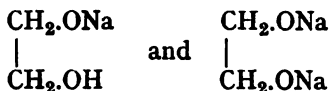
They may be esterified with organic or inorganic acids, the esterification taking place in two stages :



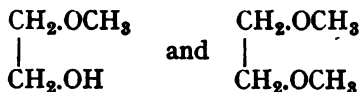
Esterification with hydrochloric acid takes place likewise in two stages :



Glycols are also capable of forming mono- and disodium derivatives :

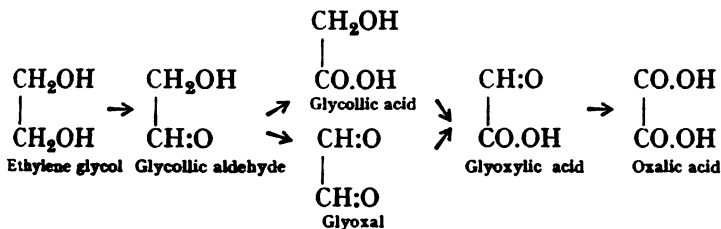


from which the corresponding alkyl ethers, such as :



can be obtained by the action of alkyl halides.

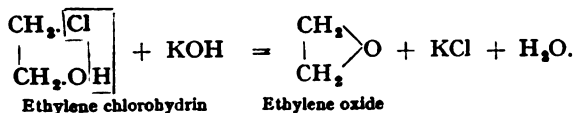
Like ethyl alcohol, ethylene glycol may be oxidised in more than one stage, but, owing to the presence of two hydroxyl groups, the number of possible intermediate oxidation-products is greater. The following table shows the possibilities :



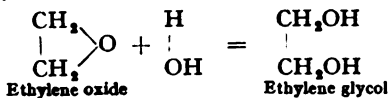
All these products are known.

Ethylene glycol is a viscous colourless liquid, miscible in all proportions with water and alcohol, insoluble in ether, and possessing a sweet taste. It boils at 195° . The striking differences between ethyl alcohol and ethylene glycol are to be ascribed to the presence of two hydroxyl groups.

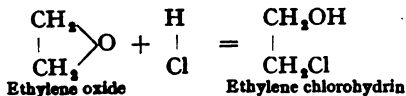
An interesting property of the first stage of the action of hydrochloric acid—ethylene chlorohydrin—is that of yielding an *internal ether* on treatment with potassium hydroxide :



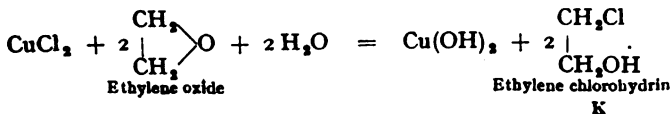
This substance is termed **ethylene oxide**, and is a mobile liquid boiling at 14° . It is highly reactive, uniting with water to form ethylene glycol :



and with hydrogen chloride, regenerating ethylene chlorohydrin :



So eagerly, in fact, does ethylene oxide unite with hydrochloric and other acids, that it causes the precipitation of the hydroxides of heavy metals when added to aqueous solutions of their chlorides :



K

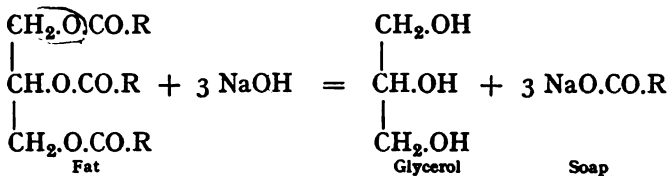
It cannot be prepared directly by dehydration of ethylene glycol.

Ethylene oxide falls into the class—members of which we shall often meet with later—of *cyclic* compounds. In these substances the atoms are arranged, as the name implies, in the form of a *ring* or *closed chain*.

Similar in properties to ethylene glycol are the isomeric substances **propylene glycol** $\text{CH}_3\text{.CHOH.CH}_2\text{.OH}$, and **trimethylene glycol** $\text{CH}_2\text{.OH.CH}_2\text{.CH}_2\text{.OH}$, both of which are prepared by hydrolysis of the corresponding halogen compounds (p. 104).

TRIHYDROXYLIC ALCOHOLS

The chief representative of this class of polyhydroxylic alcohols is the simplest member, **glycerol** $\text{CH}_2\text{.OH.CH.OH.CH}_2\text{.OH}$. This important substance, generally known as "glycerine," is produced in large quantities as a by-product in the manufacture of soap. Soap is obtained by the action of *alkalies* on fats, and consists of alkali metallic salts of saturated or unsaturated monocarboxylic acids of high molecular weight; fats are esters of such acids and glycerol. The reaction underlying soap manufacture may therefore be thus expressed:

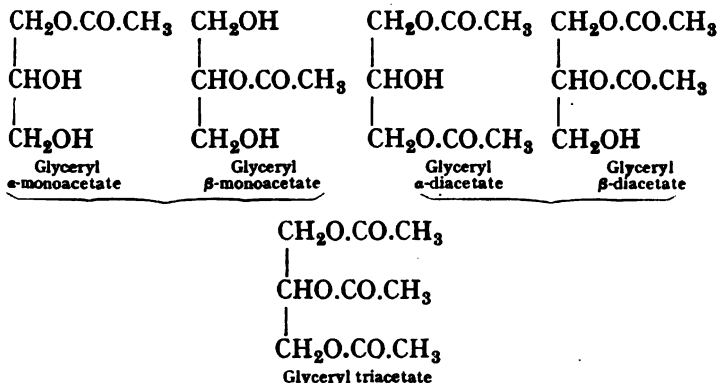


whereby it is seen to be nothing else than the hydrolysis of an ester by an alkali.

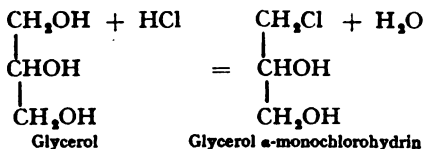
Glycerol is a viscous, colourless, odourless liquid of sweetish taste, which can be distilled without decomposition only under reduced pressure. Like ethylene glycol, it is miscible with water and alcohol, and insoluble in ether. It is highly hygroscopic. When quite pure, it can be solidified at a low temperature to a crystalline mass which melts at 17° .

It possesses all the properties ascribable to a compound containing three alcoholic hydroxyl groups: for instance, it

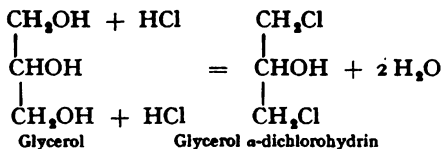
yields three classes of esters, in which one, two, or three hydroxyl groups are combined with an acid radicle :



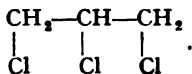
Similarly, the three hydroxyl groups can be replaced by halogen atoms. On passing gaseous hydrochloric acid into glycerol at 100° , *glycerol α -monochlorohydrin* is produced :



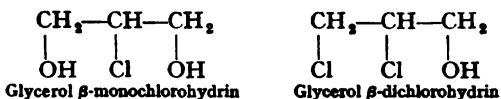
If the hydrogen chloride be passed into glycerol at 130° , *glycerol α -dichlorohydrin* is formed :



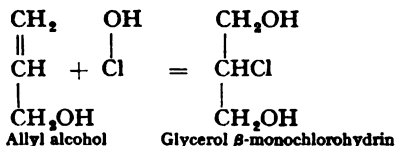
The third hydroxyl group can be exchanged for chlorine by the action of phosphorus trichloride upon glycerol or its chlorohydrins. The product is "glycerol trichlorohydrin," more correctly termed *α - β - γ -trichloropropane*



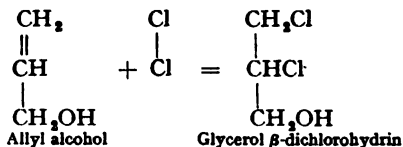
As will be understood on examination of the formulæ, second isomers of the above mono- and di-chlorohydrins can exist :



These are produced only in small quantity by the direct action of hydrogen chloride upon glycerol. The first is prepared by the action of hypochlorous acid upon allyl alcohol (cf. p. 126) :

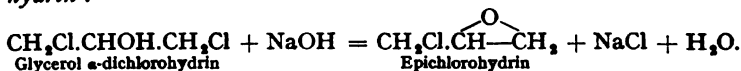


The second can be obtained by the addition of chlorine to allyl alcohol :

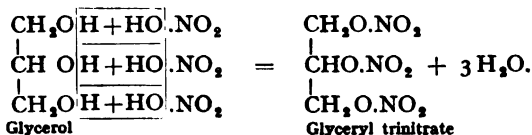


The glycerol chlorohydrins are viscous liquids, soluble in water. Their properties resemble less and less those of glycerol as the hydroxyl groups are successively replaced by chlorine atoms. α,β,γ -Trichloropropane is a typical halogenated saturated hydrocarbon : it is insoluble in water, soluble in ether, and can be distilled without decomposition.

On treating glycerol dichlorohydrin with alkalis, an internal ether analogous to ethylene oxide is produced. This is *epichlorohydrin* :



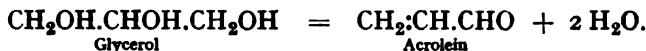
An important ester of glycerol is its trinitrate : this is produced by the action of a cold mixture of concentrated nitric and sulphuric acids upon glycerol :



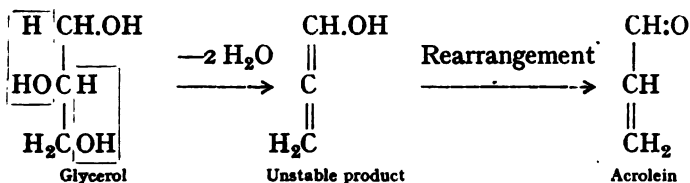
It is a heavy oil, insoluble in water. On account of its violently explosive nature it finds technical application, being known as "nitroglycerine" (p. 194).

Glycerol is capable, as is to be expected, of forming many different oxidation-products. The most important are *glyceric acid* $\text{CH}_2\text{OH}.\text{CHOH}.\text{COOH}$, *tartronic acid* $\text{COOH}.\text{CHOH}.\text{COOH}$, and *dihydroxyacetone* $\text{CH}_2\text{OH}.\text{CO}.\text{CH}_2\text{OH}$. In the formation of these it will be seen that different alcoholic groups are attacked by the oxidising agent.

The action of dehydrating agents upon glycerol is instructive. On heating glycerol with potassium hydrogen sulphate, *acrolein*, the unsaturated aldehyde corresponding with allyl alcohol, is produced :

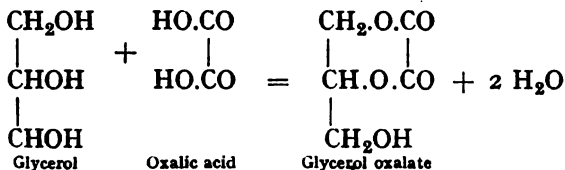


It may well be that the reaction follows some such course as this :

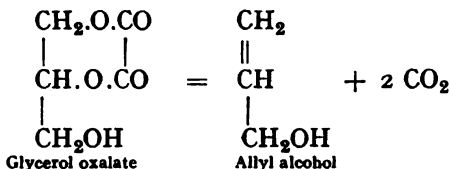


The change of the system $>\text{C}:\text{CHOH}$ to $>\text{CH}.\text{CH}:\text{O}$ is here assumed ; such a rearrangement of linkages is of frequent occurrence in organic chemistry.

It was above stated that allyl alcohol is prepared by distilling oxalic acid with an excess of glycerol. The reaction may be regarded as proceeding as follows : oxalic acid (p. 184), the simplest acid containing two carboxyl ($-\text{COOH}$) groups, reacts with the glycerol to form a cyclic ester :



This ester breaks down on strongly heating, yielding allyl alcohol and carbon dioxide :



Many higher polyhydroxylic alcohols are known. Of these **erythritol** $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$; **arabitol** and **xylitol**, which are stereoisomeric (see p. 255) forms of $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$; and **dulcitol**, **mannitol**, and **sorbitol**, stereoisomeric forms of



may be enumerated. The causes to which the possibility of stereoisomerism is ascribed are connected with the asymmetry of certain of the carbon atoms in the straight chain. Thus in the pentahydroxylic alcohols the carbon atoms printed in heavy type will, on inspection, be seen each to be united with four different groups :

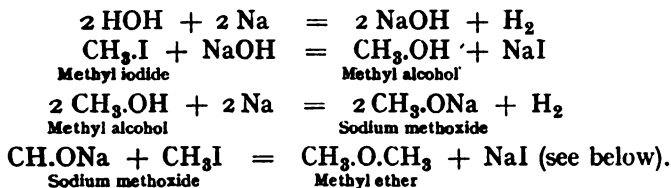


That they are all normal (straight-chain) compounds is shown by the fact that they yield reduction-products known to contain normal chains. Thus erythritol, on heating with hydriodic acid, yields secondary *n*-butyl iodide $\text{CH}_3.\text{CH}_2.\text{CHI}.\text{CH}_3$. Dulcitol, mannitol, and sorbitol all yield a mixture of β -iodo-*n*-hexane $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CHI}.\text{CH}_3$ and γ -iodo-*n*-hexane $\text{CH}_3.\text{CH}_2.\text{CHI}.\text{CH}_2.\text{CH}_3$, both of which, on reduction with zinc, yield normal hexane $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3$.

CHAPTER VIII

ETHERS

Just as an alcohol may be regarded as water in which one hydrogen atom in the molecule is replaced by an alkyl group, so can an ether be considered to be an alcohol in which the hydrogen atom attached to oxygen is replaced by a second alkyl group. The successive substitution of hydrogen atoms by alkyl groups may be shown by the following set of reactions :



Thus in structure ethers bear to alcohols a relation analogous to that which oxides bear to hydroxides.

MODES OF PREPARATION OF ETHERS

Ethers may be prepared :

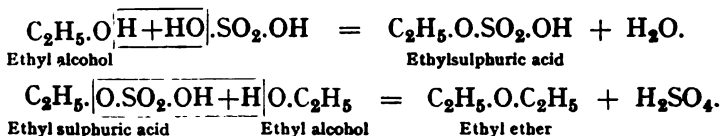
(1) By passing the vapour of an alcohol over finely-divided aluminium oxide at a suitable temperature (cf. p. 31). Thus ethyl ether is produced on passing the vapour of ethyl alcohol over finely-divided alumina at 250–260° :



As the alumina does not appear among the end-products of the reaction, and as a limited amount of it can convert

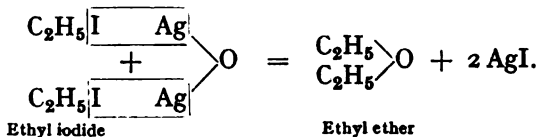
an unlimited amount of alcohol into ether, this process is said to be a "catalytic" one; under which definition the question is left open as to whether the dehydration is brought about merely by surface action or whether an intermediate product is momentarily formed and immediately decomposed.

(2) By distilling a mixture of an alcohol and sulphuric acid, the temperature being lower than in the formation of ethylenes (p. 80). The course followed by this reaction has been accurately determined: the acid is at first half esterified with the alcohol, forming, in the case of ethyl alcohol, ethyl-sulphuric acid:

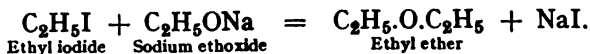


Since the sulphuric acid is regenerated in its entirety, a relatively small amount of acid can be employed for the preparation of a large quantity of ether, by adding the alcohol in a slow stream to the reacting mixture. This is known as the "continuous etherification process."

(3) By the interaction of alkyl halides with dry silver oxide:

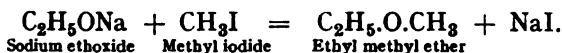


(4) (Williamson's synthesis.) By allowing an alkyl halide to act upon a metallic alkoxide:



These last two syntheses (3) and (4), show clearly the constitution (the way in which the various atoms are related to one another) of the ethers. The latter method is particularly adapted to the formation of the so-called "mixed" ethers,

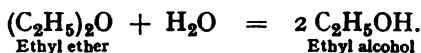
in which the alkyl groups attached to the same oxygen atoms are not identical :



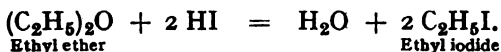
GENERAL AND CHEMICAL CHARACTERISTICS OF ETHERS

Ethers are more volatile and less soluble in water than the corresponding alcohols, and in general properties they resemble, more than any other class of compound, the saturated hydrocarbons. They are unchanged by alkalis under all conditions, and are not attacked in the cold by dilute acids and phosphorus pentachloride. Metallic sodium and potassium are without action upon them, owing to the absence of hydrogen atoms directly attached to oxygen.

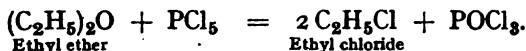
On prolonged heating with dilute acids they are slowly converted into the corresponding alcohols by hydrolysis :



With hot concentrated aqueous hydriodic acid they yield alkyl iodides :



A similar reaction takes place on heating with phosphorus pentachloride, alkyl chlorides being formed

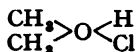


Ethers are soluble in concentrated sulphuric acid, and may be recovered unchanged on diluting such a solution with water. On prolonged heating to 100°, however, an ether dissolved in sulphuric acid is decomposed, with the formation of alkyl-sulphuric acids and alcohols :

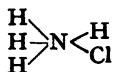


The oxygen atom in ethers can behave as if it were capable of taking up two extra valencies. Thus at low temperatures methyl

ether combines with hydrogen chloride, yielding a compound to which the constitution :



has been assigned. Such a compound is termed an *oxonium salt*, analogous to an ammonium salt :



and in recent years many substances containing oxygen in a quadrivalent condition have been observed.

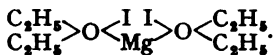
Methyl ether CH_3OCH_3 is a gas boiling at -24° under atmospheric pressure. It may be prepared by heating a mixture of sulphuric acid and methyl alcohol. It is also produced by the catalytic dehydration of methyl alcohol by heated aluminium oxide. It is readily soluble in cold concentrated sulphuric acid, and is given off again on diluting such a solution with water.

Methyl ether finds no great application either in the laboratory or in technical practice.

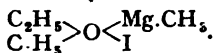
Ethyl ether $\text{C}_2\text{H}_5\text{O.C}_2\text{H}_5$, the "ether" of everyday parlance, may be prepared on a small scale by heating a mixture of equal quantities of ethyl alcohol and concentrated sulphuric acid to about 140° , and supplying fresh alcohol as rapidly as the ether so formed distils off. It is a colourless, mobile, volatile liquid, boiling at 35° . Its odour is characteristic and not unpleasant.

It finds wide application in the laboratory as a solvent of organic substances, and owing to its sparing solubility in water (at 20° , water can dissolve about 6 per cent. of ethyl ether, while the ether takes up about 1 per cent. of water) many organic substances can be removed from aqueous solution or suspension by shaking with ether, when the required solute passes into the upper ethereal layer of liquid and can be isolated by separating the liquids and distilling off the ether. This process is termed *extraction with ether*. Ethyl ether is largely employed in surgery as an anæsthetic.

Just as methyl ether can form a "hydrochloride" $(\text{CH}_3)_2\text{O} \cdot \text{HCl}$, so does ethyl ether form a number of oxonium salts, such as a hydriodide $\begin{smallmatrix} \text{C}_2\text{H}_5 & & \text{H} \\ & \diagdown & / \\ & \text{O} & \\ & / & \diagdown \\ \text{C}_2\text{H}_5 & & \text{I} \end{smallmatrix}$, and a bromide $\begin{smallmatrix} \text{C}_2\text{H}_5 & & \text{Br} \\ & \diagdown & / \\ & \text{O} & \\ & / & \diagdown \\ \text{C}_2\text{H}_5 & & \text{Br} \end{smallmatrix}$. Of interest in this connection is the product $\text{MgI}_{1.2}(\text{C}_2\text{H}_5)_2\text{O}$, formed on the addition of iodine to a suspension of magnesium in ethyl ether, and to which the following formula is assigned :



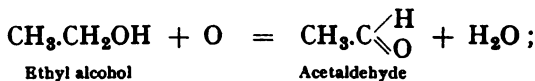
Similarly, alkyl magnesium halides (Grignard's reagents, p. 235) always exist in combination with the ether in which they are prepared :



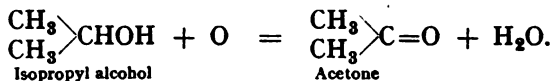
CHAPTER IX

ALDEHYDES AND KETONES

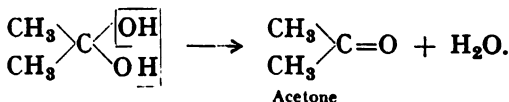
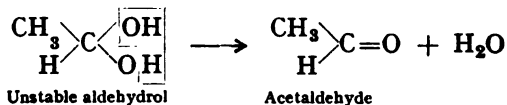
ALDEHYDES are the first product of oxidation of primary alcohols :



Ketones are derived in a similar manner from secondary alcohols :



They may alike be regarded as the anhydrides of dihydroxylic alcohols in which both hydroxyl groups are attached to one and the same carbon atom :

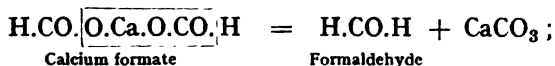


The difference between aldehydes and ketones is that in the former at least one hydrogen atom is attached to the carbonyl (>C:O) group, while in the latter the carbonyl group is directly united with two carbon atoms.

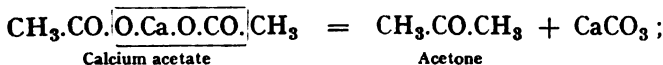
As was indicated in the opening chapters, there are many types of reactions common to both classes, but since direct attachment to a carbonyl group confers certain characteristic properties upon a hydrogen atom, aldehydes may be considered independently of ketones. This difference, though less marked, is in some measure comparable to the difference between alcohols and ethers. We may, however, first take up those points which aldehydes and ketones have in common.

FORMATION OF CARBONYL COMPOUNDS

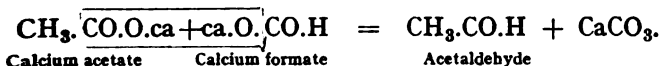
In addition to the oxidation of alcohols, carbonyl compounds may be prepared by the dry distillation of the calcium salts of carboxylic acids. Thus calcium formate, on distillation, yields formaldehyde :



calcium acetate yields acetone :

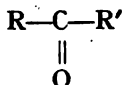


calcium propionate $(\text{C}_2\text{H}_5\text{.CO.O.})_2\text{Ca}$ yields diethyl ketone $(\text{C}_2\text{H}_5)_2\text{C:O}$; and so on. Aldehydes in general may be produced by distilling an equimolecular mixture of a calcium salt of a carboxylic acid with calcium formate; in order to simplify the equation we may write "ca" to represent a hypothetical univalent half-atom of calcium :

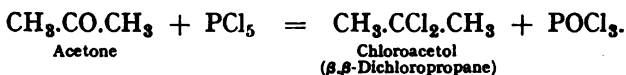
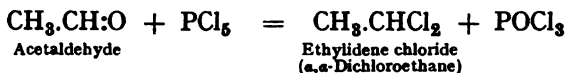


GENERAL REACTIONS OF CARBONYL COMPOUNDS

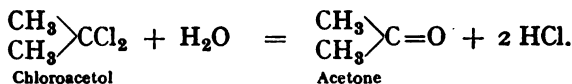
Compounds containing the grouping



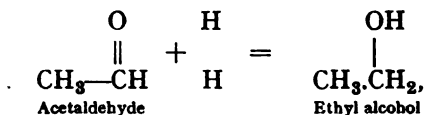
(where R and R' may be either alkyl groups or hydrogen atoms, or one of each), react with phosphorus pentachloride, yielding a dichloro-derivative of a hydrocarbon, in which the two chlorine atoms are attached to the same carbon atom :



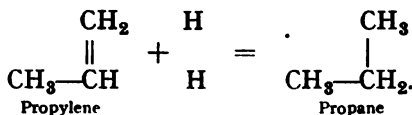
These halogen derivatives on hydrolysis regenerate the original aldehyde or ketone :



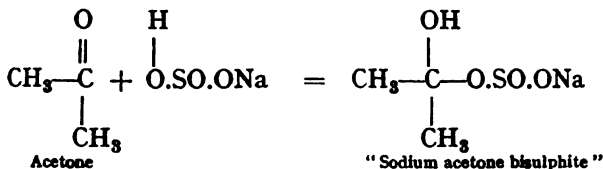
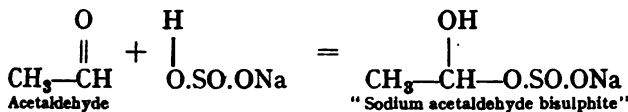
Carbonyl compounds, which all contain an oxygen atom doubly bound to a carbon atom ($>\text{C=O}$), resemble unsaturated compounds, (*e.g.* $\text{CH}_2=\text{CH}_2$), in that they are capable of forming additive compounds. Thus with nascent hydrogen they are reduced to alcohols :



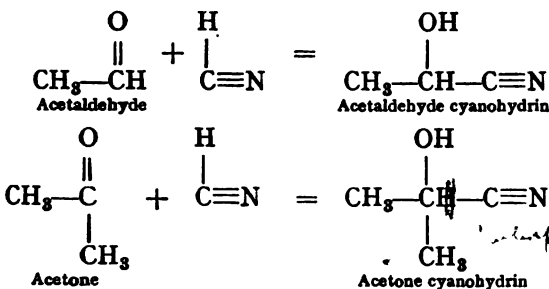
a reaction analogous to :



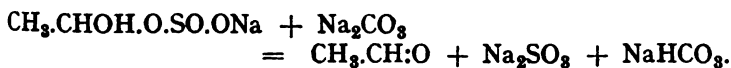
The parallelism fails in the action of halogens and hydrogen halides, since the reactions follow a different course (p. 145), but carbonyl compounds are able to form well-defined addition-products with other substances. The most important of these are sodium hydrogen sulphite (sodium bisulphite) :



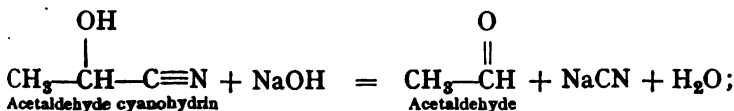
and hydrogen cyanide :



The "bisulphite compounds" are crystalline solids which are soluble in water, but sparingly soluble in a concentrated solution of sodium hydrogen sulphite. They are decomposed, with regeneration of the original carbonyl compound, on boiling with aqueous sodium carbonate :

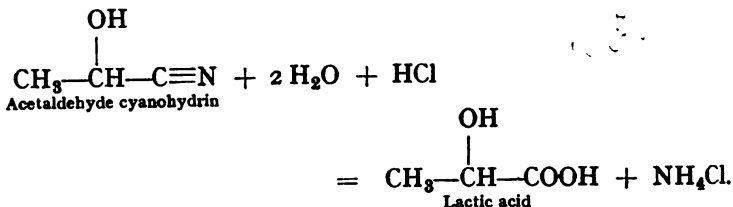


The cyanohydrins may be broken up in a similar manner with alkalis :

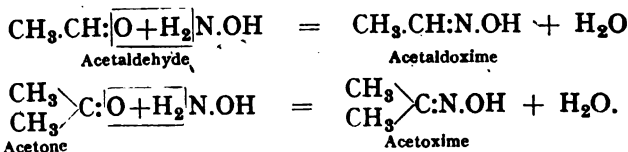


with concentrated mineral acids they are hydrolysed in the

manner of nitriles (p. 220), yielding ammonia and hydroxy-acids (p. 241) :

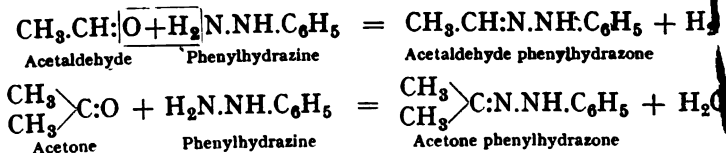


Carbonyl compounds possess further the faculty of exchanging their oxygen atom with certain other groups ; for instance, with hydroxylamine NH_2OH they yield a type of compound designated by the generic term oxime (i.e. hydroxy-imino compound) :

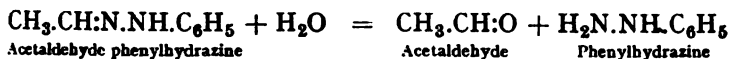
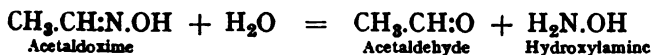


An oxime from an aldehyde is termed an *aldoxime*, an oxim from a ketone is called a *ketoxime*.

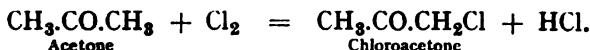
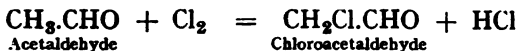
A similar reaction takes place with hydrazine NH_2NH_2 and certain of its substitution-products. The derivative of hydrazine most generally employed is a substance known *phenylhydrazine*, which has the formula $\text{C}_6\text{H}_5\text{NH.NH}_2$ (p. 378) :



The resulting condensation products are termed *hydrazones*. Oximes and hydrazones, on boiling with dilute acids, are hydrolysed, the original carbonyl compound being formed :

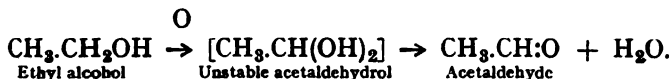


With halogens, substitution takes place very readily in aldehydes and ketones, the hydrogen atoms attached to the carbon atom next to the carbonyl group being replaced :



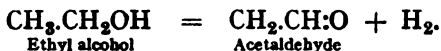
FORMATION OF ALDEHYDES

The most general method of preparation of aldehydes is the oxidation of primary alcohols by means of warm aqueous chromic acid or similar oxidising agents :

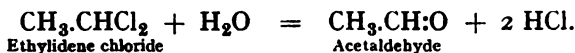


They may also be prepared by the direct oxidation of the primary alcohol by atmospheric oxygen in presence of some catalyst such as spongy platinum, or by hot copper oxide.

On passing the vapour of a primary alcohol over finely-divided copper at 300°, a mixture of the corresponding aldehyde and hydrogen is produced :



A method of theoretical interest is the hydrolysis of *α,α*-dichloro- or dibromo-substituted hydrocarbons :

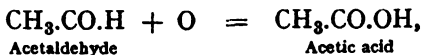


Finally, traces of aldehydes are produced on heating a mixture of oxygen with certain saturated hydrocarbons to a temperature lower than that necessary to bring about complete combustion.

REACTIONS PECULIAR TO ALDEHYDES

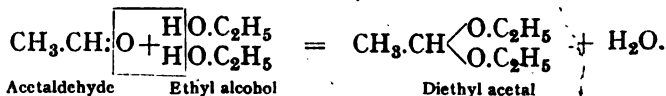
Aldehydes, whilst giving the principal reactions common to ketones, are capable of undergoing several other chemical changes; for not only do they differ from the latter in possessing a hydrogen atom directly bound to the carbonyl group, but the carbonyl group itself in an aldehyde is capable of entering into a few reactions which are not given by ketones.

Aldehydes are readily oxidised to acids:

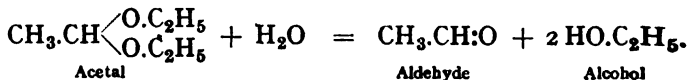


by oxidising agents which are without effect upon ketones.

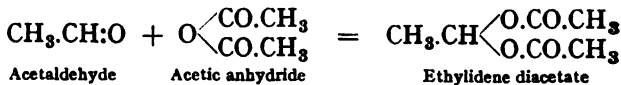
On heating an aldehyde with an alcohol, preferably in presence of a small quantity of hydrogen chloride, sulphuric acid or phosphoric acid, condensation takes place, yielding an *acetal*, or ether in which two alkoxyl ($-\text{O.C}_n\text{H}_{2n+1}$) groups are attached to the same carbon atom:



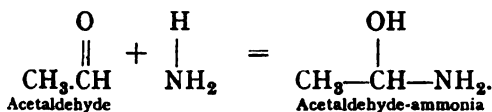
An acetal is thus a di-alkyl ether of the unstable hydrated form of an aldehyde: R.CH(OH)_2 . Acetals may be hydrolysed, with regeneration of aldehyde and alcohol, by boiling with dilute mineral acid:



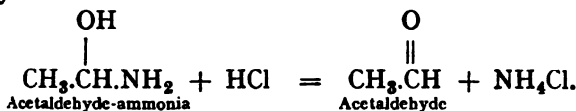
A similar reaction takes place with carboxylic acid anhydrides:



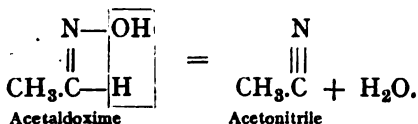
With ammonia, *aldehyde-ammonias* are produced from all simple aldehydes except formaldehyde (p. 148):



These are decomposed by dilute acids, with regeneration of the aldehyde :



The oximes of aldehyde—aldoximes—are dehydrated on treatment with acetic anhydride, acetyl chloride, phosphorus pentoxide, and similar reagents, *nitriles* (p. 220) being formed :



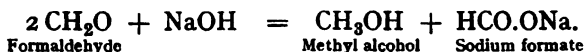
PREPARATION AND PROPERTIES OF INDIVIDUAL ALDEHYDES

The first member of the aldehyde series is **formaldehyde** CH_2O . It is a gas of pungent and suffocating odour, and can be condensed to a liquid boiling at -20° . It is produced technically by the flameless oxidation of methyl alcohol by atmospheric oxygen in presence of heated spongy platinum or copper, such finely-divided metals acting catalytically as "contact agents."

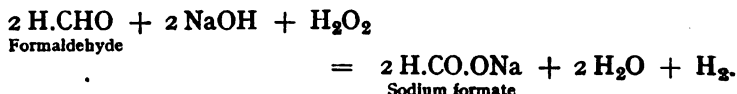
It is very soluble in water : a 40 per cent. solution is largely employed in technical and medical practice for disinfectant, preservative, and other purposes, under the name "Formalin." This aqueous solution of formaldehyde probably contains the stable dihydroxymethane or *formaldehydrol* $\text{CH}_2(\text{OH})_2$.

Formaldehyde polymerises readily with formation of products of high molecular weight. The most important of these is *polyoxymethylene*, sometimes incorrectly termed "trioxymethylene," a white crystalline solid, from which formaldehyde is regenerated on heating.

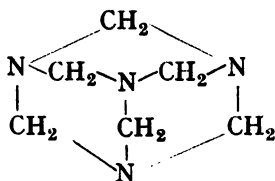
On treatment with alkali, formaldehyde undergoes a singular intermolecular change, by which methyl alcohol and formic acid is produced :



It is completely converted into formic acid on treatment with alkali and hydrogen peroxide, hydrogen being evolved :



With ammonia, an aldehyde-ammonia is not produced, but a product free of oxygen—called *hexamethylenetetramine*— $\text{C}_6\text{H}_{12}\text{N}_4$ is formed. This product, to which the formula :



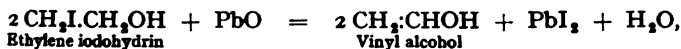
is assigned, is decomposed again into formaldehyde and ammonia on boiling with dilute acids.

The properties of **acetaldehyde** $\text{CH}_3\text{CH}_2\text{O}$, are typical of aliphatic aldehydes ; formaldehyde—as is frequently the case with the initial members of homologous series—displays properties differing somewhat from those of the succeeding members.

Acetaldehyde is a colourless volatile liquid, of characteristic odour, boiling at 21° . It is miscible in all proportions with water. It can be prepared either by warming a mixture of ethyl alcohol with aqueous chromic acid or by passing acetylene into a solution of mercuric chloride acidified with hydrochloric acid.

A further interesting mode of formation is that of heating ethylene iodohydrin $\text{CH}_2\text{I.CH}_2\text{OH}$ (cf. p. 128) with lead oxide. It

is assumed that the elements of hydrogen iodide are first removed by the lead oxide, yielding *vinyl alcohol*, an unstable isomer of acetaldehyde :

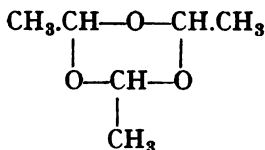


which at once undergoes an intramolecular isomeric transformation into acetaldehyde :



by the shifting of the position of a hydrogen atom (cf. p. 133).

Acetaldehyde, like formaldehyde, is prone to polymerisation. Only in a state of high chemical purity can it be preserved for an indefinite length of time ; in the presence of traces of impurities, such as acids, it slowly passes into the polymeric **paraldehyde** ($\text{C}_2\text{H}_4\text{O}$)₃, to which the constitution :



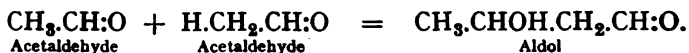
is assigned. This polymerisation takes place with considerable evolution of heat on adding a drop of concentrated sulphuric acid. Paraldehyde is a colourless liquid, of pleasant odour, boiling at 124°, which possesses no aldehydic properties, in that it is not readily oxidised and forms no addition-compounds with sodium hydrogen sulphite, etc. It resembles rather an acetal, since acetaldehyde is regenerated on boiling with dilute mineral acids.

A higher degree of polymerisation is brought about by warming acetaldehyde with concentrated aqueous alkalis, an intensely aromatic resinous substance, "aldehyde resin," being produced.

A different type of polymerisation is effected by the action of a small quantity of dilute alkali, or zinc chloride. The product in this case possesses the formula $(\text{C}_2\text{H}_4\text{O})_2$, and has been shown to possess the structure expressed by :



It is a true aldehyde which also contains an alcoholic hydroxyl group, and is formed by the transference of a hydrogen atom in one molecule of acetaldehyde to another member of acetaldehyde :

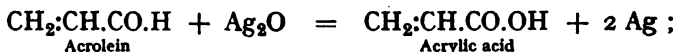


It is known as **aldol**, and the type of reaction involved in the formation is termed an *aldol-condensation*.

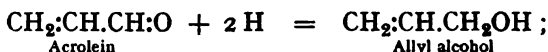
Of the addition-products of acetaldehyde, the most important are acetaldehyde sodium bisulphite $\text{CH}_3\text{.CHOH.O.SO.ONa}$, and acetaldehyde-ammonia $\text{CH}_3\text{.CHOH.NH}_3$; these are solids which can readily be isolated, and can thus serve for the purification of the aldehyde. The cyanohydrin is notable in that on hydrolysis with concentrated hydrochloric acid it yields the important substance lactic acid (p. 243); it is hence sometimes termed *lactonitrile*.

UNSATURATED ALDEHYDES

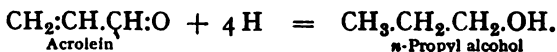
The most important unsaturated aldehyde is **acrolein** (or **acraldehyde**) $\text{CH}_2\text{:CH.CH:O}$, formed by heating glycerol with potassium hydrogen sulphate. The mechanism of this reaction has already been discussed on p. 133. Acrolein is a volatile mobile liquid, of highly pungent odour, boiling at 52° . On oxidation with silver oxide it yields acrylic acid (p. 168) :



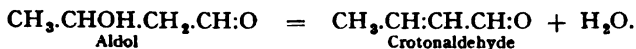
on reduction it passes into allyl alcohol (p. 126) :



and it shows its unsaturated character by the formation of the compounds $\text{CH}_2\text{Br.CHBr.CH:O}$ and $\text{CH}_2\text{Br.CH}_2\text{.CHO}$ on treatment with bromine and hydrogen bromide respectively. On vigorous reduction it yields normal propyl alcohol :



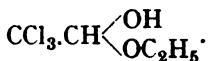
Crotonaldehyde $\text{CH}_3\text{CH}:\text{CH}\cdot\text{CHO}$ is a compound of similar properties, boiling at 104° . It is readily produced by heating aldol :



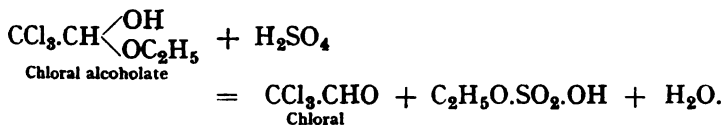
HALOGEN-SUBSTITUTED ALDEHYDES

Just as the hydrogen atoms in methane can be replaced by halogen atoms, so can the hydrogen atoms in aldehydes be substituted. It is possible to obtain monochloro-, dichloro-, and trichloro-derivatives of acetaldehyde; of these the only important member is *trichloroacetaldehyde* $\text{CCl}_3\cdot\text{CHO}$, generally known as **chloral**.

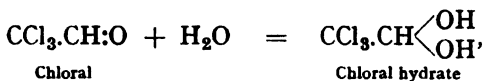
Chloral cannot be prepared by the direct action of chlorine upon acetaldehyde, but is formed on passing chlorine into ethyl alcohol, whereby a compound of chloral and ethyl alcohol, known as *chloral alcoholate*, is produced, which has the constitution :



On distillation with concentrated sulphuric acid, the alcohol is removed, chloral itself passing over :

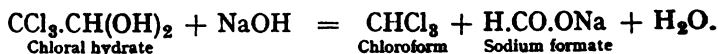


Chloral is a liquid which boils at 98° . It combines with water, with evolution of heat, to form *chloral hydrate* :

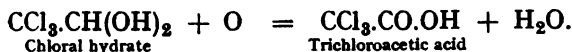


a white crystalline solid, melting at 57° , which is a true aldehydrol or α,α -dihydroxylic alcohol. The exceptional stability of this aldehydrol group is due to the strongly electro-negative character of the group— CCl_3 .

Chloral hydrate is employed in medicine as a hypnotic. On warming with alkalis it yields chloroform and formic acid :

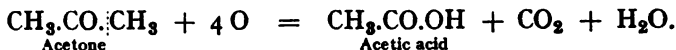


On oxidation it yields trichloroacetic acid :

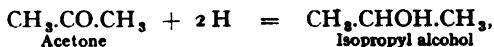


REACTIONS PECULIAR TO KETONES

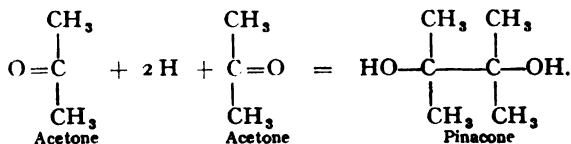
As before stated, ketones are far less readily oxidised than aldehydes. When they are treated with powerful oxidising agents, such as a hot alkaline solution of permanganate, one of the linkages between the carbonyl group and the carbon atoms is ruptured. Thus, for example, acetone yields acetic acid and carbon dioxide :



On reduction, besides yielding the corresponding secondary alcohol :



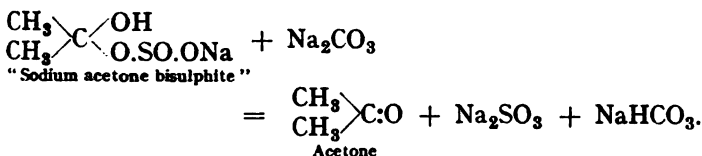
ketones undergo a curious condensation by which a *ditertiary glycol* (termed a "pinacone"). Thus acetone yields *pinacone*, or tetramethyl ethylene glycol :



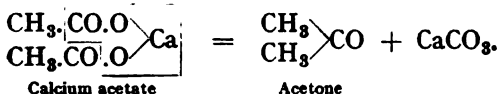
PREPARATION AND PROPERTIES OF INDIVIDUAL KETONES

The most important of all ketones is the simplest :— **acetone** $\text{CH}_3\text{.CO.CH}_3$. It is obtained in large quantities as a

by-product in the manufacture of methyl alcohol by destructive distillation of wood (p. 113). For purification, the crude acetone so obtained is treated with a concentrated solution of sodium hydrogen sulphite, and the crystalline bisulphite compound collected and decomposed by boiling with a strong solution of sodium carbonate :



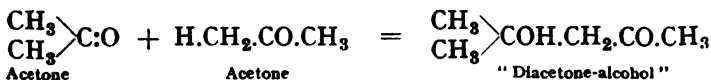
It is also prepared by the dry distillation of crude calcium acetate in a current of superheated steam :



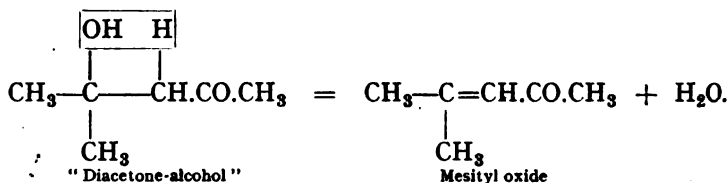
It occurs in urine during diabetes and in other pathological conditions, and has recently been shown to be produced by the action of certain bacteria on starch.

Acetone is a colourless, volatile liquid, boiling at 57° , of agreeable odour, and miscible in all proportions with water. It is largely employed in the laboratory and in technical practice as a solvent. As above stated, it is far less readily oxidisable than acetaldehyde; an illustration of this is the fact that acetone is capable of dissolving potassium permanganate without any reaction taking place between the solute and solvent.

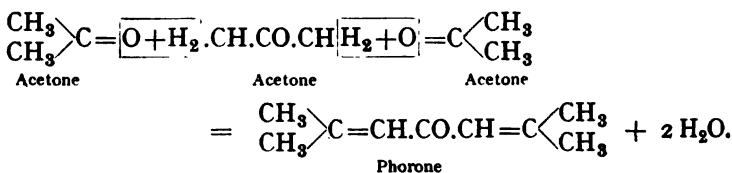
Acetone shows no tendency to polymerise in the way that acetaldehyde does; on the other hand, condensation can readily be effected by means of certain substances. Thus, on treatment with concentrated sodium hydroxide solution, an *aldol condensation* (p. 150) is brought about :



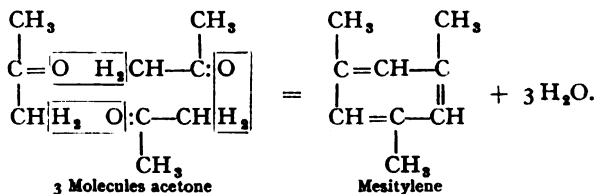
yielding "**diacetone-alcohol**," which on dehydration yields **mesityl oxide**, an unsaturated ketone :



In the same way, three molecules of acetone can condense together, yielding **phorone**, a doubly unsaturated ketone :



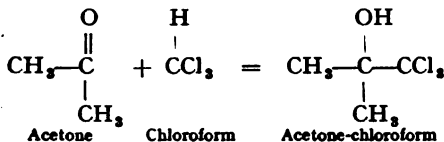
There is another way in which three molecules of acetone may condense. On treating acetone with concentrated sulphuric acid, a hydrocarbon called *mesitylene* (p. 317), containing nine carbon atoms, is produced :



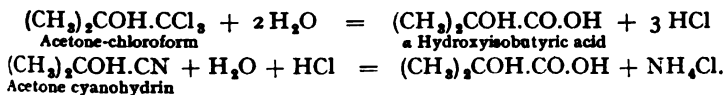
This hydrocarbon is of especial interest in connection with the chemistry of aromatic compounds (see p. 300).

On treatment with sodium hypochlorite, acetone yields chloroform (p. 101) ; with iodine and alkali, iodoform (p. 103) is produced. The mechanism of these reactions has already been discussed.

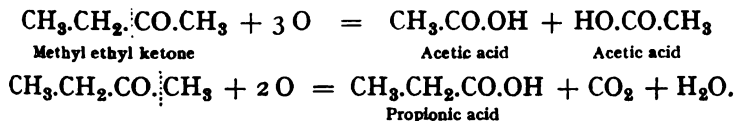
A curious condensation-product of acetone with chloroform, known as *acetone-chloroform*, can be prepared by warming a mixture of acetone, chloroform, and aqueous potassium hydroxide :



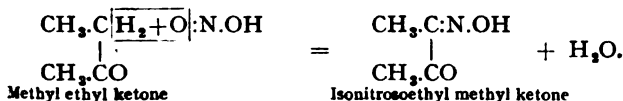
As will be seen from the formula, it is a trichloro derivative of tertiary butyl alcohol (p. 117). It is a stable camphor-like solid, which melts at 97°. On heating with water it yields a carboxylic acid, containing an alcoholic hydroxyl group (p. 241), identical with that produced by hydrolysis of acetone cyanohydrin :



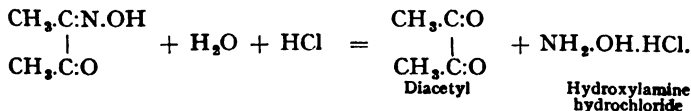
Higher ketones, homologues of acetone, occur in the higher-boiling fractions of acetone manufacture. The most important of them is **methyl ethyl ketone** $\text{CH}_3\text{CO.CH}_2\text{CH}_3$. This is a liquid which boils at 78° and closely resembles acetone. On oxidation it yields a mixture of acetic and propionic acids :



Methylene ($>\text{CH}_2$) groups attached to the carbonyl group in ketones are readily attacked by various reagents, which replace the two hydrogen atoms by elimination of water. Thus methyl ethyl ketone reacts with nitrous acid, yielding an *isonitroso* derivative :



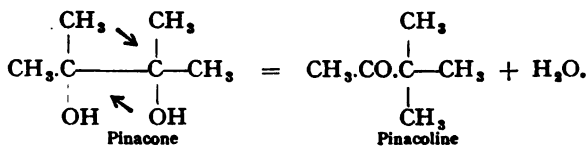
As will be seen from the formula, the term *isonitroso derivative* is synonymous with *oxime* (p. 144). On hydrolysis with dilute mineral acids, isonitrosoethyl methyl ketone yields hydroxylamine and the diketone **diacetyl** :



An interesting member of the ketone series is **pinacolone** or *methyl tertiary-butyl ketone* :



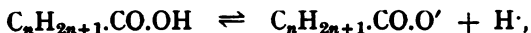
This is produced, by a curious rearrangement of atoms, on boiling pinacone (p. 152) with dilute acids :



CHAPTER X

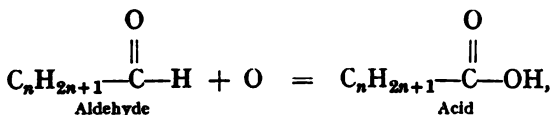
SIMPLE MONOCARBOXYLIC ACIDS AND THEIR DERIVATIVES

IN organic chemistry, as in inorganic chemistry, the criterion of an acid is the presence in its aqueous solution of hydrogen ions, a condition which can be demonstrated in a variety of ways, chemical and physical. This condition is fulfilled among compounds containing only carbon, hydrogen and oxygen, by the carboxylic acids alone. Carboxylic acids—the simplest examples of which are the “fatty acids,”¹ consisting of a *carboxyl*² ($-\text{CO.OH}$) group attached to a hydrogen atom or an alkyl ($\text{C}_n\text{H}_{2n+1}$) radicle—are ionised in aqueous solution in the sense :



though to a far less extent than the strong mineral acids such as hydrochloric, sulphuric, and nitric.

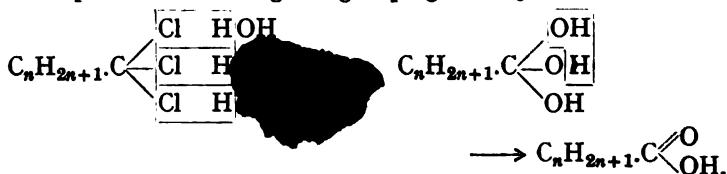
The constitution of the carboxylic acids is evident from their formation by oxidation of aldehydes :



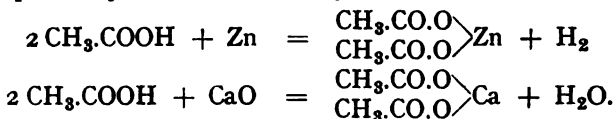
¹ The term “fatty acid” is derived from the fact that the first members of the series $\text{C}_n\text{H}_{2n+1}.\text{COOH}$ to be accurately investigated were obtained by hydrolysis of fats (esters of glycerol, p. 130).

² The word *carboxyl* is derived from *carbonyl* and *hydroxyl*.

as well as from the fact that they are produced by the hydrolysis of compounds containing the grouping $-\text{CCl}_3$:



In the carboxyl group we come across a phenomenon of the greatest importance in organic chemistry—namely the *mutual influence* of different groups in the same molecule. In the carboxyl group we have both a carbonyl group ($>\text{C}=\text{O}$) and a hydroxyl radicle. The hydroxyl group in carboxylic acids is represented by the same symbol ($-\text{OH}$) as is the hydroxyl radicle in alcohols, but its association with the carbonyl group has altogether altered its character from that of an alcoholic hydroxyl. Alcohols are neutral bodies, which have no effect upon, for instance, metallic zinc or quicklime. Carboxylic acids, exemplified by acetic acid, readily react with these substances :



Similarly, the carbonyl group is, by its association with the hydroxyl group, altered in character from that of the carbonyl group in aldehydes or ketones. A carboxylic acid forms neither "bisulphite compound," cyanohydrin, oxime, nor hydrazone.

We must therefore take all these facts into account when reading the meaning into the symbol $-\text{COOH}$, and must regard the properties of the complex radicle as that of a single individual group.

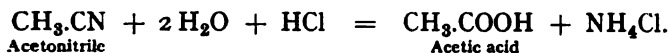
PREPARATION AND PROPERTIES OF SIMPLE SATURATED CARBOXYLIC ACIDS AND THEIR IMMEDIATE DERIVATIVES

The modes of preparation based upon the oxidation of primary alcohols or aldehydes (pp. 107, 146) have already been mentioned.

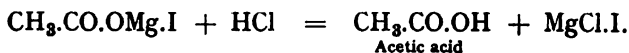
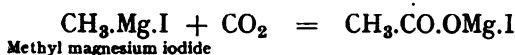
Carboxylic acids may also be prepared by the hydrolysis of nitriles (p. 220): an alkyl halide is allowed to interact with potassium cyanide, whereby the nitrile, or alkyl cyanide, is produced:



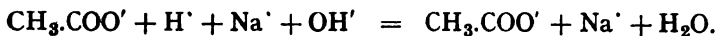
On heating with aqueous mineral acids, these nitriles are hydrolysed, yielding ammonia and a fatty acid containing one carbon atom more than the original alkyl halide:



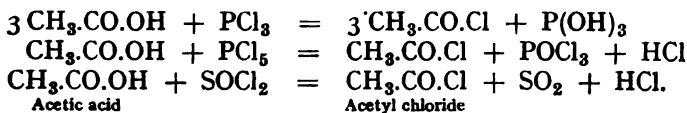
Another method is to treat an alkyl magnesium halide (p. 236) such as methyl magnesium iodide CH_3MgI , with carbon dioxide, and decomposing the addition-product with dilute acid:



Carboxylic acids, on treatment with alkalis or alkali carbonates, form salts, the aqueous solutions of which are neutral and contain positive and negative ions:



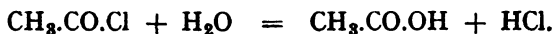
On treatment with phosphorus trichloride, phosphorus pentachloride, thionyl chloride, and similar halides of inorganic acid radicles, they are converted into their halides:



Acetic acid

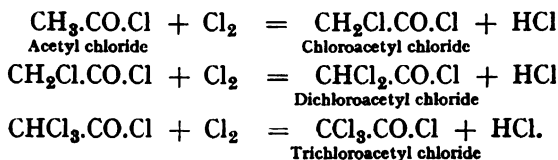
Acetyl chloride

On treatment of acid halides with water, the free acids are regenerated:

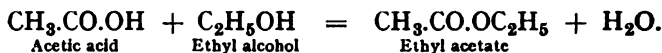


Halogens react slowly with carboxylic acids, but more readily with their halides. Thus acetyl chloride is successively

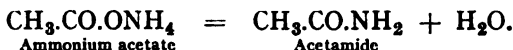
chlorinated to monochloroacetyl, dichloroacetyl, and trichloroacetyl chlorides :



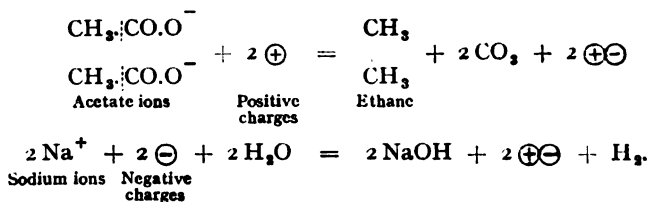
On heating a mixture of an alcohol and a carboxylic acid, *esterification* (p. 32) takes place :



On heating an ammonium salt of a carboxylic acid, an *amide* is produced :



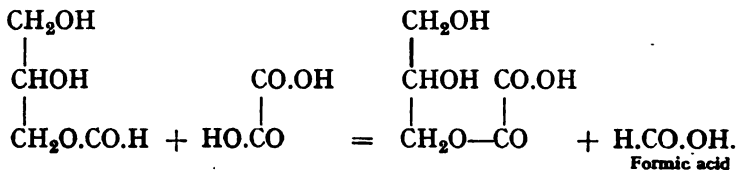
When an electric current is passed through an aqueous solution of a metallic salt of a carboxylic acid, such as sodium acetate, the electrolytic decomposition does not follow the course usual in the case of inorganic compounds. Hydrogen is evolved at the cathode, whilst carbon dioxide and a hydrocarbon collects at the anode. In the case of sodium acetate, ethane is produced :



INDIVIDUAL FATTY ACIDS

At ordinary temperatures, the lower members of the fatty acid series are liquids which are miscible with water and possess sharp penetrating odours. Those containing four to nine carbon atoms in the molecule are oils of unpleasant odour, only slightly soluble in water ; whilst fatty acids containing ten

The glyceryl monoformate reacts with more oxalic acid, whereby free formic acid and glyceryl hydrogen oxalate are formed :



The process then repeats itself, until the supply of oxalic acid is exhausted. A limited amount of glycerol, therefore, is capable of converting an unlimited amount of oxalic acid into formic acid.

Of theoretical interest is the formation of formic acid by the hydrolysis of chloroform with dilute alkali :

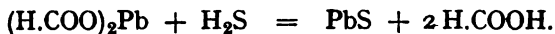


and of hydrogen cyanide with dilute acids :



Here the hydrocyanic acid functions as the *nitrile* (p. 219) of formic acid.

The formic acid obtained by the above methods may be concentrated by fractional distillation ; but as it, like alcohol, forms a constant-boiling mixture with water, anhydrous formic acid cannot be so obtained. This mixture, which contains 77.5 per cent of formic acid, boils at 107°, or 6° higher than the anhydrous acid. For the preparation of the pure acid, lead carbonate is added to the aqueous acid, and the lead salt separated, dried, and heated to about 110° in a current of hydrogen sulphide :

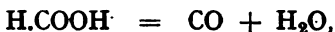


The dry acid, which distils over, is purified by redistillation.

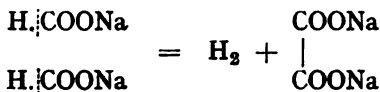
Formic acid is a colourless substance, which melts at 8° and boils at 101°, and is miscible in all proportions with water, alcohol, ether, and many other liquids. It has no pronounced odour, but its vapour is highly pungent, and attacks the mucous membranes. It is the strongest (*i.e.* dissociated to the greatest

extent in aqueous solution) of all the simple mono-carboxylic acids.

The two methods of preparation based upon the hydration of carbon monoxide and removal of carbon dioxide from oxalic acid, can be reversed by suitable treatment of formic acid. Thus if formic acid be warmed with concentrated sulphuric acid, carbon monoxide is quantitatively disengaged :



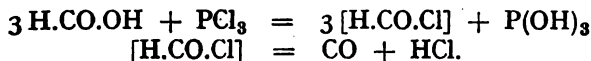
this reaction forming the most convenient process for the preparation of pure carbon monoxide. On heating an alkali formate to above 400° in absence of air, hydrogen is evolved, with production of alkali oxalate :



Formic acid differs from other fatty acids in being readily oxidisable. Like acetaldehyde, it reduces silver and cupric salts :



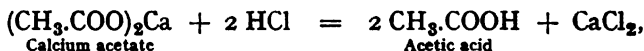
This is of course due to the presence of a hydrogen atom which is comparable to the "carbonyl" hydrogen atom in aldehydes : —CO.H . It may here be noted that formic acid is incapable of forming a chloride, since this breaks up at once into carbon monoxide and hydrogen chloride :



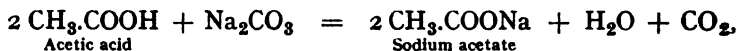
Similarly, formic anhydride H.CO.O.CO.H has never been isolated. The amide, formamide H.CO.NH_2 (p. 174), is on the other hand a well-defined and stable substance ; and many esters H.CO.OR of formic acid are known.

Acetic acid CH_3COOH , the acid principle of vinegar, is, as has already been stated (p. 113), prepared in large quantities from the products of the destructive distillation of wood, the acid being removed by neutralisation with slaked

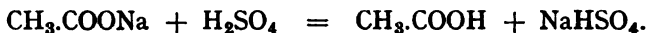
lime. The crude calcium acetate so obtained (the "gray lime" of commerce) is treated with a quantity of concentrated hydrochloric acid just sufficient to decompose it according to the equation :



and the mixture distilled. Dilute acid containing some 50 per cent. of water is thus obtained. This is neutralised with sodium carbonate :



and the resulting sodium acetate isolated by evaporation to dryness, and subsequently heated in order to expel water of crystallisation, since sodium acetate crystallises with three molecules of water : $\text{CH}_3\text{.COONa} \cdot 3 \text{H}_2\text{O}$. It is to be noted that, unlike calcium acetate, sodium acetate can be heated to fusion without decomposition. The dry sodium acetate is mixed with concentrated sulphuric acid and distilled, whereby pure anhydrous acetic acid passes over :

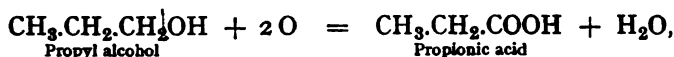


Acetic acid, and all other fatty acids except formic acid, may be warmed with concentrated sulphuric acid without decomposition. It is a colourless crystalline substance, melting at 16° ("Glacial" acetic acid), and boiling at 118° , and is miscible with water and many organic liquids. The odour is characteristic and pungent. Acetic acid is employed in technical practice as a solvent, and, in aqueous solution, as a weak acid.

Vinegar is the dilute acetic acid produced by the oxidation of wine and other alcoholic liquors. The oxidation, which air alone is unable to effect, is brought about by a living organism (*Mycoderma aceti*) which is present in beech-wood. Vinegar is now usually prepared by the "quick vinegar process," in which the dilute alcohol (wine, beer, etc.) is allowed to trickle over beech-wood shavings, which afford a large surface for oxidation and contain supplementary nutriment for the organism. The temperature is maintained at about 35° , and

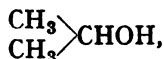
the access of air is carefully regulated, since if the oxidation proceed too rapidly, the alcohol is oxidised to carbonic acid. The process is repeated with the liquor which has passed through, until all the alcohol is oxidised.

Propionic acid $\text{CH}_3\cdot\text{CH}_2\cdot\text{COOH}$, usually prepared by the oxidation of propyl alcohol :



is a liquid closely resembling acetic acid. It melts at -22° and boils at 141° .

Butyric acids $\text{C}_3\text{H}_7\cdot\text{COOH}$. Just as there exist two alcohols $\text{C}_3\text{H}_7\text{OH}$ —normal propyl alcohol $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, and isopropyl alcohol



—so are there two butyric acids—normal butyric acid

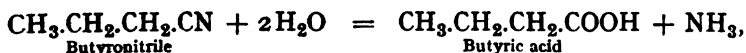


and isobutyric acid



Normal butyric acid $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ occurs in rancid butter. It is produced in quantity by the fermentation of solutions of glucose (p. 275) under the action of the "butyric acid ferment" contained in decomposing cheese or meat. To prepare butyric acid by this method, a solution of glucose is mixed with a small quantity of putrid cheese and some calcium carbonate. The mixture is then allowed to stand for a few days at about 30° . The calcium carbonate neutralises the acid as rapidly as it is produced, so that the fermentation takes place in neutral solution.

Synthetical methods, as for instance hydrolysis of normal butyronitrile (propyl cyanide) :

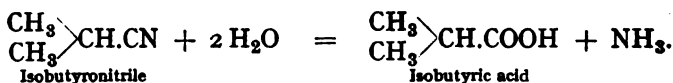


also lead to the formation of normal butyric acid ; but the chief

method of preparation in technical practice involves the use of the butyric acid ferment.



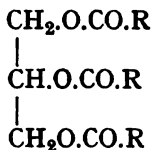
does not occur among the products of the acid fermentation of sugars. The principal methods of preparation are therefore synthetical ones, as for instance from isobutyronitrile (isopropyl cyanide) :



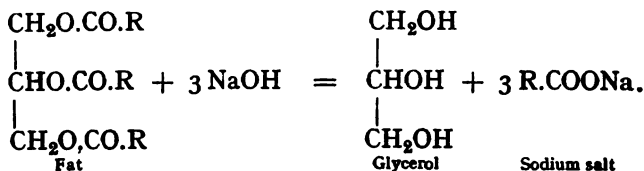
Both butyric acids are liquids of extremely unpleasant odour. Normal butyric acid melts at -8° and boils at 162° , and is miscible in all proportions with water. Isobutyric acid melts at -79° and boils at 154° ; it is not completely miscible with water.

Of the fatty acids of higher molecular weight the most important are **palmitic acid** $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ and **stearic acid** $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$. These occur in almost all fats as esters of glycerol.

Fats are all mixtures of esters of glycerol, or *glycerides* (p. 130) :



and on boiling with alkalis, they are hydrolysed ("saponified"), yielding free glycerol and the corresponding salts of the acids :



The salts of these higher fatty acids are the chief constituents of soaps. When sodium hydroxide is employed for saponification, the ordinary hard sodium soaps are produced; the potassium

salts form "soft soap." Most animal fats consist chiefly of mixtures of the glycerides of palmitic and stearic acids ; hence common soap consists principally of a mixture of sodium palmitate $C_{15}H_{31}.COONa$ and sodium stearate $C_{17}H_{35}.COONa$.

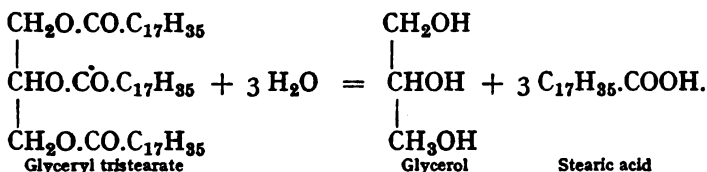
On the addition of mineral acid to a soap solution the free fatty acids are precipitated :



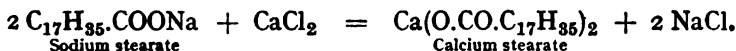
Palmitic acid and stearic acid are white waxy crystalline solids of low melting points, which are absolutely insoluble in water, and hence do not give an acid reaction to litmus paper moistened with water. The acid reaction, however, is shown when the litmus paper is moistened with alcohol.

A mixture of these higher fatty acids is employed for the manufacture of the so-called "stearin" candles, as the free acids melt at a higher temperature than do the corresponding glycerides.

In the technical preparation of these acids from fats, hydrolysis is brought about by heating the fat in a current of superheated steam, whereby glycerol and the fatty acids are set free :



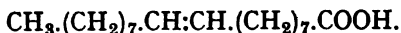
Metallic salts of these acids, other than those of the alkali salts, such as those of calcium or magnesium, are insoluble in water. For this reason "permanently hard" waters, containing inorganic salts of calcium and magnesium, do not form a lather unless an excess of soap is added :



UNSATURATED MONOCARBOXYLIC ACIDS

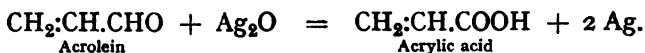
These acids are derived from unsaturated hydrocarbons by substitution of a carboxyl group for a hydrogen atom, just as

the saturated acids are derived from paraffins by replacing an atom of hydrogen by a carboxyl group. The only members of the series $C_nH_{2n-1}.COOH$ which need here be noted are acrylic acid $CH_2:CH.COOH$, and oleic acid

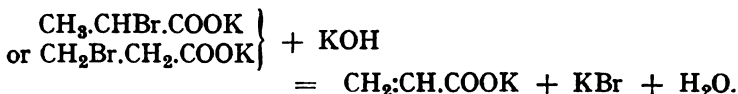


These acids behave in every way like the corresponding saturated fatty acids, with the difference that they display in addition the normal characteristics of ethylenic compounds.

Acrylic acid $CH_2:CH.COOH$ is produced by the oxidation of acrolein (p. 150) by means of silver oxide :

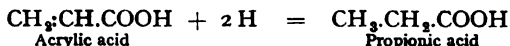


It can also be prepared by the action of alkalies upon α - or β -¹ halogen-substituted propionic acids :

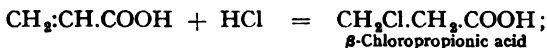


Acrylic acid is a colourless liquid, of pungent odour, which boils at about 140° ; it solidifies in a freezing mixture to a crystalline mass melting at 13° .

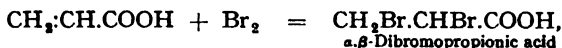
On reduction, by treatment in aqueous solution with sodium amalgam, it yields propionic acid :



With hydrogen chloride it yields β -chloropropionic acid :

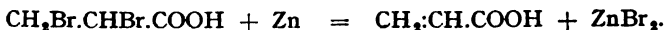


and with bromine it yields dibromopropionic acid :



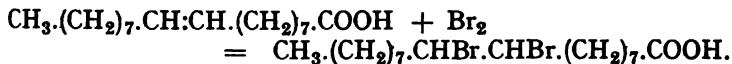
¹ When a substituent atom or group—in this case halogen—is attached to the same carbon atom as the carboxyl group, the prefix α - is employed to denote its position. Thus $CH_3.CHCl.COOH$ is α -chloropropionic acid; $CH_2Cl.CH_2.COOH$ is termed β -chloropropionic acid. If the substituent lie even further from the carboxyl group, the prefixes γ -, δ -, ϵ -, etc. are employed, as circumstances may demand.

which, on treatment with zinc, is reconverted into acrylic acid :



Oleic acid $\text{CH}_3.(\text{CH}_2)_7.\text{CH}:\text{CH}.\text{CH}_2)_7.\text{COOH}$ occurs in certain fats as its glyceride (*olein*) which forms in particular the chief constituent of olive oil, whence its name. It is a colourless oil, which solidifies in a freezing mixture and melts at 14° . Its sodium and potassium salts form soapy solutions in water.

On reduction it is converted into palmitic acid, and it is capable of uniting with halogens :

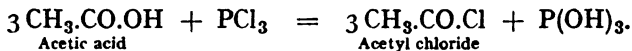


The proportion of olein (together with other unsaturated glycerides) in fats is estimated in technical analysis by the amount of iodine chloride which a weighed amount of fat is capable of absorbing. Iodine chloride itself—or a mixture of mercuric chloride and iodine, which may be regarded as containing free iodine chloride—is dissolved in alcohol and the amount of free halogen per litre in this standard solution determined by adding excess of potassium iodide and titrating with sodium thiosulphate. A known volume of this solution is mixed with a solution of the fat in chloroform, and allowed to stand in the dark for twelve hours, after which the unabsorbed halogen is estimated by titration. The amount of halogen, expressed as the number of grams of iodine which 100 grams of a fat is capable of absorbing, is known as the *iodine number* of the fat.

ACID HALIDES

The most important of these are the *chlorides*, which contain the radicle $-\text{CO}.\text{Cl}$.

They are generally prepared by the action of phosphorus trichloride upon the free acid :



Phosphorus tribromide gives rise to the corresponding acid bromides.

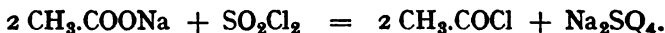
Another method, which possesses the advantage of yielding no non-volatile by-products, is to treat the acid with thionyl chloride SOCl_2 :



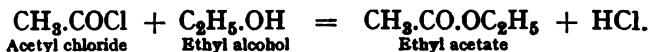
A third general method of preparation involves the action of phosphorus pentachloride upon a metallic salt of an acid :



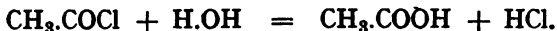
For the technical preparation of acid chlorides on a large scale, sulphuryl chloride SO_2Cl_2 (prepared by the interaction of chlorine and sulphur dioxide in presence of a catalyst) is allowed to act upon salts of organic acids :



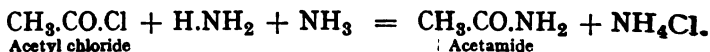
Acid chlorides react with substances containing an alcoholic hydroxyl group, yielding the *acyl* derivative of the alcohol and hydrogen chloride :



When acetyl chloride is so employed, the process is known as *acetylation*. The simplest substance containing a hydroxyl group—water—reacts in the same way, yielding the free acid and hydrogen chloride :



With ammonia and substances containing a hydrogen atom attached to a tervalent nitrogen atom, acyl derivatives are also formed. In the case of ammonia, the product is an *amide* :



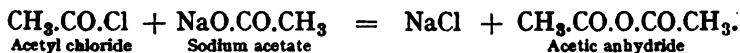
Formyl chloride $\text{H}.\text{CO}.\text{Cl}$ is unknown, as all attempts to prepare it have led to the formation of carbon monoxide and hydrogen chloride only (p. 163).

Acetyl chloride $\text{CH}_3.\text{CO}.\text{Cl}$ is a colourless, volatile, pungent liquid, boiling at 51° . It fumes on exposure to air, owing to its decomposition by the atmospheric moisture.

Owing to the readiness with which it reacts with substances containing alcoholic hydroxyl radicles it is largely employed for the detection of such groups, the formation of an acetyl derivative being indicative of the presence of an alcoholic hydroxyl group. **Acetyl bromide** $\text{CH}_3\text{CO.Br}$ is a liquid boiling at 76° , which closely resembles acetyl chloride.

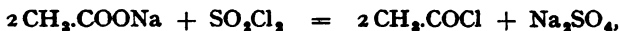
ACID ANHYDRIDES

When an acid chloride is heated with a metallic salt of the same acid, a double decomposition takes place, whereby the metallic atom is replaced by an acyl group:



Such a compound is termed an **acid anhydride**.

In technical manufacture of acid anhydrides, as for instance, acetic anhydride, sulphuryl chloride SO_2Cl_2 is passed over a heated metallic acetate, whereby acetyl chloride is first formed:

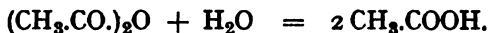


which then reacts with a further quantity of the acetate:

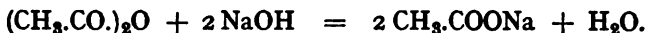


so that the anhydride is obtained in one operation.

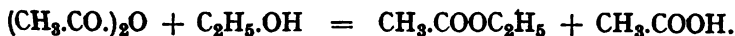
Pure acid anhydrides are insoluble in cold water, but gradually enter into solution. This is due to their decomposition into the free acid:



This hydrolysis is more rapidly effected by heating with water or dilute alkali:



Acid anhydrides may also be employed, like acid chlorides, for *acylation* of compounds containing alcoholic hydroxyl groups:

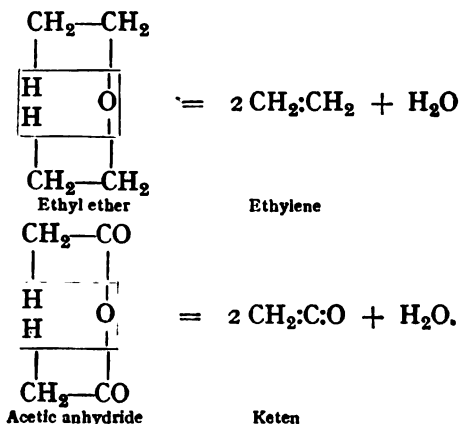


In this reaction one of the *acid radicles* (e.g. $\text{CH}_3\text{CO}-$) behaves in the manner of the chlorine atom in acid chlorides.

Formic anhydride H.CO.O.CO.H , as above noted (p. 163), is unknown.

Acetic anhydride $\text{CH}_3.\text{CO.O.CO.CH}_3$ is a colourless oil of peculiar odour, which boils at 136° . It is largely employed in the laboratory and in technical practice as an acetylating agent.

If a platinum wire, placed in acetic anhydride, be electrically heated to dull redness, a variety of gaseous products is obtained, the most important constituent of which is **keten** $\text{CH}_2:\text{CO}$. Its relation to acetic anhydride is comparable to that of ethylene to ethyl ether :



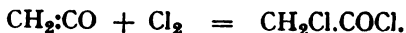
Keten is a colourless gas, of suffocating odour, which can be condensed to a liquid boiling at -56° . It reacts energetically with water and other hydroxylic substances, and can therefore be employed as an acetylating agent :



With hydrogen chloride it yields acetyl chloride :

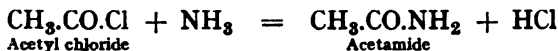


and with chlorine it yields chloroacetyl chloride :



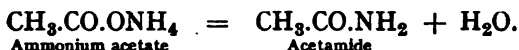
ACID AMIDES

Just as acid chlorides and acid anhydrides react with water, replacing one of the hydrogen atoms by an acid radicle, so do they react, even more energetically, with ammonia :

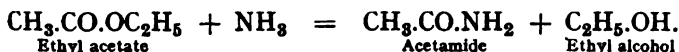


The free acid thereby liberated combines, of course, with more ammonia, forming ammonium chloride or the ammonium salt of the organic acid. The resulting *acyl derivatives* of ammonia are termed **acid amides**.

Acid amides, as already stated, are also formed on heating the ammonium salts of carboxylic acids :

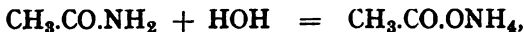


Another method for their preparation consists in treating an ester with ammonia :

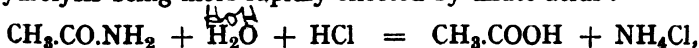


Acid amides are neutral bodies, for the most part white crystalline solids at ordinary temperatures. Their neutrality towards litmus is interesting, and shows the effect of the association of the basic nitrogen atom with the acid radicle.

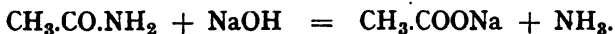
They are converted into ammonium salts on prolonged heating with water :



hydrolysis being more rapidly effected by dilute acids :

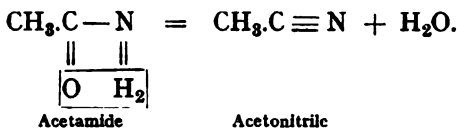


or alkalies :

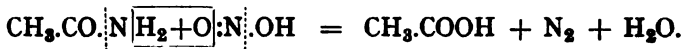


On treatment with powerful dehydrating agents, such as phosphorus pentoxide, they yield *nitriles* (p. 220), identical

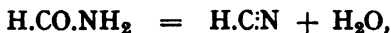
with the products of the interaction of alkyl halides with potassium cyanide :



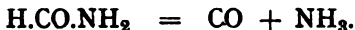
By the action of nitrous acid upon amides, the corresponding carboxylic acid is produced, nitrogen being evolved.



Formamide $\text{H}\cdot\text{CO}\cdot\text{NH}_2$ melts at 3° and boils between 192° and 195° . On heating to its boiling-point it is partially decomposed, yielding water and hydrogen cyanide :



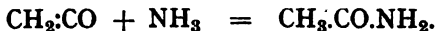
as well as ammonia and carbon monoxide :



It is a colourless liquid, miscible with water.

Acetamide $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$ is a white crystalline solid which melts at 82° and boils at 223° . It is soluble in water and in most organic liquids.

It is formed by all the general methods above enumerated ; in addition, it is quantitatively produced by the interaction of ammonia and keten :



ESTERS

Enough has already been stated concerning the structure of esters, or acyl derivatives of alcohols, to make clear their constitution as organic analogues of salts. In chemical character, however, esters of carboxylic acids differ fundamentally from salts of carboxylic acids, and partake to some extent of the nature of ethers.

Salts, as is well known, dissolve for the most part in water, yielding ionised solutions, from which, by evaporation of the

water, they can be obtained unchanged. Esters, on the other hand, are as a rule but slightly soluble in water, and exhibit no signs of electrolytic dissociation.

The difference can perhaps best be summarised by comparing salts and oxides :

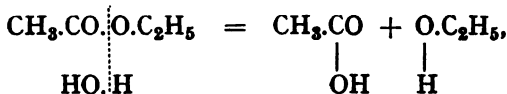


in contrast to esters and ethers :

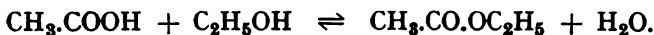


In other words, esters constitute a more inert type of compound than salts.

This similarity is, however, not fully borne out, for it is possible to cause esters to react with water, resulting in rupture of the linkage between the acid radicle and the alcoholic group :



Esters are obtainable by heating together a mixture of equivalent quantities of a carboxylic acid and an alcohol, *esterification* ensuing by elimination of water. This reaction is reversible ; it may hence be written (in the case of acetic acid and ethyl alcohol) :

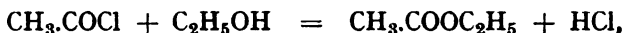


The meaning of this is that if equivalent quantities of alcohol and acid be heated until no further reaction takes place (state of equilibrium), the resultant mixture will contain acid, alcohol, ester, and water, in certain definite proportions. Further, exactly the same mixture will be obtained if equivalent quantities of ester and water be heated until equilibrium is established. The state of equilibrium obtains when the acid and alcohol are being esterified exactly as fast as the ester is being hydrolysed.

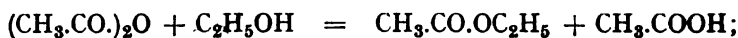
It has been found experimentally that the above mixture is in equilibrium when two-thirds of the acid and alcohol have reacted to form the ester. It has also been found that the

presence of a small quantity of concentrated sulphuric acid or gaseous hydrogen chloride shifts the equilibrium point in such a way that the final reaction mixture consists almost wholly of ester and water ; from this we must infer that the acid either accelerates esterification or retards hydrolysis. For this reason, in order to obtain a good yield of ester, it is customary to add a few drops of concentrated sulphuric acid to the mixture of acid and alcohol before heating, or to pass dry hydrogen chloride into the heated mixture.

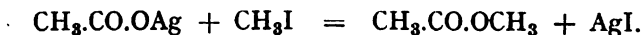
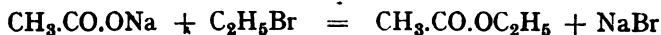
Other methods of preparing esters are the interaction of alcohols with acid chlorides :



or with acid anhydrides :

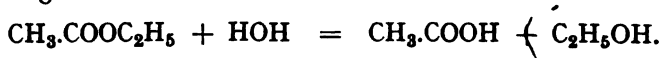


whilst an alternative method consists in treating a metallic salt of a carboxylic acid with an alkyl halide :



The most important property of esters is their capability of being hydrolysed. Much has already been said concerning this subject ; we need therefore merely summarise the methods by which hydrolysis is brought about.

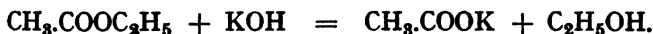
Firstly, the fact that esterification is a reversible reaction indicates that if water be present in large excess, the equilibrium point will be shifted so that the proportion of ester in the final mixture is very small. Esters can therefore be hydrolysed by heating with excess of water :



It has been found that the velocity of hydrolysis increases with the amount of ester hydrolysed ; this is due to the liberation of free acid, for the velocity of hydrolysis depends on the concentration of hydrogen ions in the water. For this reason it is advantageous to effect hydrolysis by heating with dilute

mineral acids, as in such solutions the concentration of hydrogen ions is high.

Secondly, hydrolysis of esters may be brought about by heating with aqueous or alcoholic alkalis. Here the principle is different : as fast as free acid is liberated from the ester, it is at once neutralised by the alkali, the possibility of recombining with alcohol being thus removed. The reaction thus rapidly reaches the point at which all the acid originally in the form of ester is combined with alkali :



Esters can be formed from any acid with any alcohol, so that the number of esters known is very large. A few examples will show the system of nomenclature :



Methyl formate



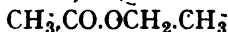
Ethyl formate



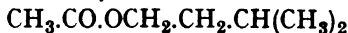
Ethyl butyrate



Methyl acetate



Ethyl acetate



Isoamyl acetate

Esters are for the most part fragrant oils, many of them occurring in nature as the odorous principles in fruits.

In addition to esters of simple alcohols, esters of polyhydroxylic alcohols are known. Such are **ethylene glycol diacetate** and **glyceryl triacetate**



As already stated, fats consist of glyceryl esters of fatty acids of high molecular weight.

CHAPTER XI

SIMPLE DICARBOXYLIC ACIDS AND THEIR DERIVATIVES

Just as alcohols containing two or more hydroxyl groups can exist, so are there acids containing more than one carboxyl group. Acids in which two carboxyl groups are present are termed *dibasic* acids, since they can combine with two equivalents of a base.

The simplest dicarboxylic acid is oxalic acid, in which two carboxyl groups are directly joined :



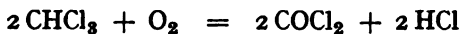
but before considering this acid and its homologues, the derivatives of carbonic acid, though not strictly a dicarboxylic acid, may be first discussed.



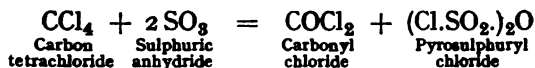
itself has never been isolated, though a solution of carbon dioxide in water behaves as if it contained hydrogen carbonate, and its salts are stable substances. The derivatives of carbonic acid resemble in many ways those of carboxylic acids, so that it is of interest here to describe some of their properties.

The chloride, **carbonyl chloride** COCl_2 , has long been known as the product obtained when a mixture of carbon monoxide and chlorine is exposed to sunlight. For this reason it has been termed "phosgene" (*generated by light*). Carbonyl

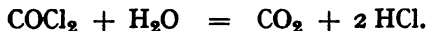
chloride is also produced by the action of light upon chloroform in presence of oxygen (p. 102) :



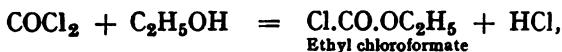
and by the action of fuming sulphuric acid upon carbon tetrachloride :



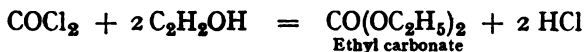
Carbonyl chloride is a gas which may be condensed in a freezing mixture to a liquid, boiling at 8° , which has a pungent and suffocating odour and a marked toxic action. On treatment with water it yields carbon dioxide and hydrogen chloride :



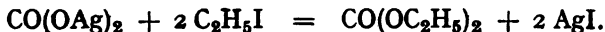
With alcohols it yields **alkyl chloroformates** (also called *alkyl chlorocarbonates*), which are liquids which combine the properties of ester and acid chloride :



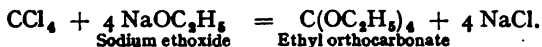
and **alkyl carbonates**, which behave as true esters :



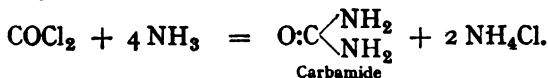
Alkyl carbonates may also be produced by the action of alkyl halides on silver carbonate :



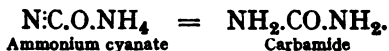
Alkyl orthocarbonates C(OR)_4 are also capable of existence. They are produced by the interaction of metallic alkoxides with carbon tetrachloride :



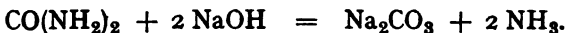
By the action of ammonia on carbonyl chloride, **carbamide** is produced :



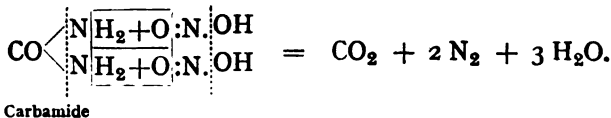
Carbamide is a white crystalline solid which melts at 132° and is readily soluble in water. It is of especial interest in that it is the chief end-product of human nitrogenous metabolism, being excreted in large quantities in the urine, from which fact it is frequently termed **urea**. It was the first organic compound to be synthesised from inorganic materials, Wöhler obtaining it in 1828, by heating a solution of ammonium cyanate (p. 223) :



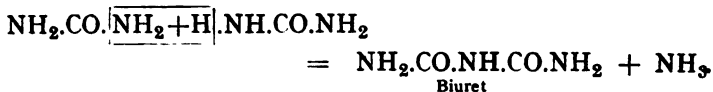
Carbamide shows its character of acid amide by yielding ammonia and sodium carbonate on prolonged boiling with aqueous sodium hydroxide :



It yields carbonic acid and nitrogen on treatment with nitrous acid :

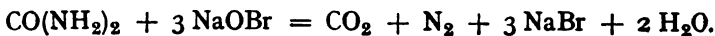


On heating alone it evolves ammonia and is converted into a more complex compound known as **biuret** :



Biuret, in alkaline aqueous solution, yields a pink coloration with a trace of copper sulphate. This, the "biuret test," serves as a test for carbamide.

In medical practice it is frequently necessary to estimate the urea in a sample of urine. The classic method of estimation consists in adding to the sample an excess of alkaline sodium hypochlorite solution, and measuring the evolved gas. Sodium hypochlorite or hypobromite oxidises carbamide, with evolution of nitrogen :



The carbon dioxide is not evolved with the nitrogen, since it combines at once with the alkali present.

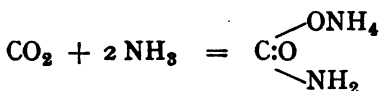
As this method is not altogether accurate, the more modern procedure is to boil the sample of urine for some time with concentrated hydrochloric acid and magnesium chloride, whereby the carbamide is hydrolysed to carbon dioxide in ammonia :



The ammonia so formed can then be estimated by rendering alkaline and distilling into standard acid, as in Kjeldahl's process (p. 59).

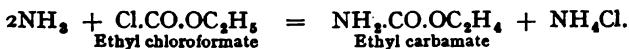
Carbamide preserves slightly basic properties, although it is neutral to litmus. It thus forms a well-defined salt with hydrochloric acid : $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$; and a nitrate $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, which is only sparingly soluble in water.

When dry carbon dioxide and ammonia are brought together, a white solid is produced, technically known as "ammonium carbonate." This is in reality the ammonium salt of the monoamide of carbonic acid, and is strictly termed **ammonium carbamate** :



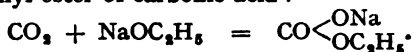
In aqueous solution, however, it is hydrolysed and behaves as the true ammonium salt of carbonic acid.

Carbamic acid itself $\text{NH}_2\text{CO.OH}$, is incapable of existence, since it at once breaks up into ammonia and carbon dioxide. Alkyl esters of this unknown acid are, however, known. Thus, **ethyl carbamate** is produced by the interaction of ammonia and ethyl chloroformate :

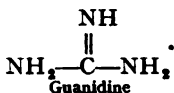


In alkyl carbamates—also termed **urethanes**—the properties characteristic both of esters and amides are united.

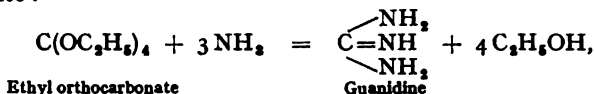
On passing carbon dioxide into alcoholic sodium ethylate, a precipitate is formed which has the composition of the sodium salt of the monoethyl ester of carbonic acid :



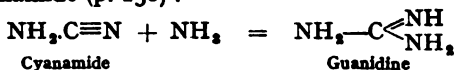
Guanidine is an important derivative of carbonic acid in which all the four valencies of the carbon atom are attached to nitrogen atoms :



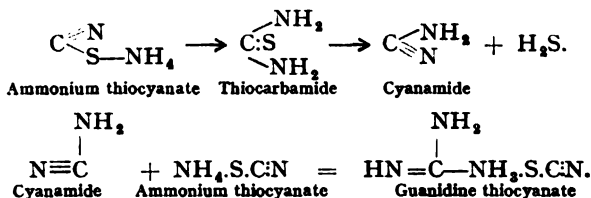
It is produced by the action of ammonia upon ethyl orthocarbonate :



or upon cyanamide (p. 230) :



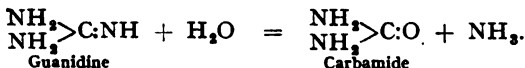
The most convenient method for its preparation is to heat ammonium thiocyanate, which first undergoes an isomeric change analogous to that of ammonium cyanate (p. 223), yielding thiocarbamide. This, on further heating, loses hydrogen sulphide with formation of cyanamide, which at once reacts with more ammonium thiocyanate, yielding guanidine thiocyanate :



Guanidine is a colourless crystalline hygroscopic solid, which possesses strongly basic properties, yielding with acids stable salts, such as guanidine hydrochloride :



On gentle hydrolysis by boiling with aqueous barium hydroxide, it yields carbamide and ammonia :



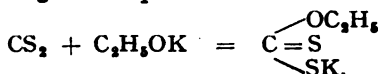
Sulphur derivatives of carbonic acid are known. The simplest are carbon disulphide $\text{C} \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix}$ and carbon oxysulphide $\text{C} \begin{smallmatrix} \text{O} \\ \text{S} \end{smallmatrix}$.

Carbon disulphide CS_2 is a colourless liquid, boiling at 46° . It is insoluble in water, and highly inflammable. It possesses a most disagreeable odour, and its vapour produces specific physiological disturbances when inhaled in large quantity. It is prepared by passing sulphur vapour over heated carbon.

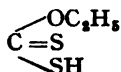
Carbon oxysulphide COS is a colourless inflammable gas of unpleasant odour. It is formed by heating a mixture of carbon monoxide and sulphur vapour :



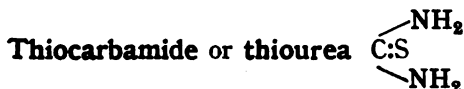
When carbon disulphide is added to alcoholic potash or potassium ethoxide, a yellow crystalline precipitate of **potassium ethyl xanthate** or **xanthogenate** is produced :



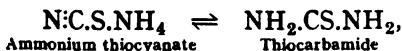
Similar substances are produced from other alcohols. The free xanthic acid



is unstable, and cannot be isolated in a pure state, as it rapidly decomposes into carbon disulphide and ethyl alcohol. When a solution of potassium xanthate is treated with copper sulphate, a brown precipitate of cupric xanthate is formed, which rapidly changes into yellow cuprous xanthate. The name "xanthate" (from *ξανθός*, yellow) is derived from this fact.



is the thio-analogue of carbamide, and is formed, in a manner analogous to the formation of carbamide (p. 223), by heating ammonium thiocyanate. This reaction is not quantitative, but rather appears to be a reversible one :



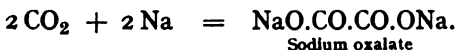
since on heating pure thiocarbamide, a certain amount of ammonium thiocyanate is regenerated. It is a stable crystalline substance which melts at 172° .

TRUE DICARBOXYLIC ACIDS

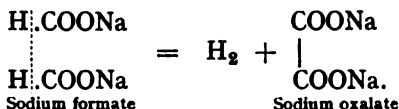


is the last product of oxidation—before carbon dioxide—of organic substances in which carbon atoms are directly united. For example, it is produced by heating sugar with strong nitric acid.

Oxalic acid may be synthesised from simpler substances in a variety of ways. On passing carbon dioxide over sodium or potassium at 360° , oxalates are produced :



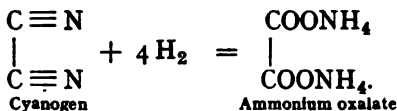
Oxalates are also formed by heating the formates of alkali metals to 440° in the absence of air :



Oxalic acid is produced by the prolonged heating of hexachloroethane (p. 103) with potassium hydroxide :



also by the hydrolysis of cyanogen (p. 222) :



Oxalic acid occurs widely in nature, calcium oxalate being a universal constituent of plant cells. The potassium hydrogen salt COOH.COOK occurs in sorrel (*Oxalis*) and some other plants.

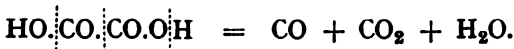
On the large scale, oxalic acid is manufactured by heating a mixture of sawdust and potassium hydroxide in shallow iron vessels to a temperature between 200° and 220° . Hydrogen is evolved in quantity during the operation. The fused mass is extracted with water, and lime-water added to the clear solution, whereby the oxalic acid is precipitated as insoluble calcium oxalate. This is then decomposed by sulphuric acid, the calcium sulphate removed, and the free acid purified by crystallisation.

Oxalic acid crystallises from water in colourless prisms, which melt at 101° . This is hydrated oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, which probably has the true hydrated (*ortho*) structure :

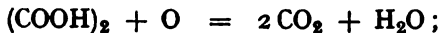


On heating above 100° the water is removed, leaving anhydrous oxalic acid, which can be sublimed.

On strongly heating alone, oxalic acid breaks down into carbon monoxide, carbon dioxide, formic acid and water. On heating with concentrated sulphuric acid, carbon monoxide and carbon dioxide are evolved :

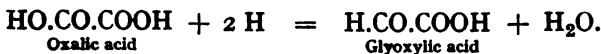


Oxalic acid is readily oxidised by a warm acid solution of permanganate :



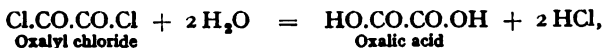
on the other hand, it is unchanged by alkaline permanganate solution. Similarly, hydrogen peroxide oxidises oxalic acid, but does not oxidise potassium oxalate.

On reduction in aqueous solution with sodium amalgam, glyoxylic acid (p. 258) is produced :

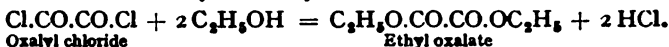


When one equivalent of anhydrous oxalic acid is treated with two equivalent quantities of phosphorus pentachloride, **oxalyl chloride** $\text{Cl} \cdot \text{CO} \cdot \text{CO} \cdot \text{Cl}$ is produced. This is a colourless liquid, which boils at 64° , and exhibits the characteristics common to

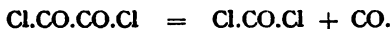
acid chlorides. Thus it is decomposed by water, yielding oxalic acid :



and with alcohols it yields alkyl oxalates :



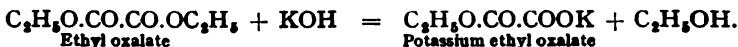
On passing the vapour through a tube heated to 600° , oxalyl chloride breaks down, yielding carbon monoxide and carbonyl chloride :



Oxalic anhydride $\begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array} \text{O}$ is unknown.

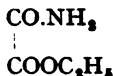
Esters of oxalic acid may be obtained by heating alcohol with anhydrous oxalic acid, and subsequently distilling. **Methyl oxalate** $(\text{COOCH}_3)_2$ is a white crystalline solid, melting at 54° and boiling at 163° . **Ethyl oxalate** $(\text{COOC}_2\text{H}_5)_2$ is an oil which boils at 185° .

Both esters are readily hydrolysed by aqueous alkalis. With alcoholic potassium hydroxide in the cold, ethyl oxalate yields an immediate precipitate of potassium ethyl oxalate, which is both salt and ester :

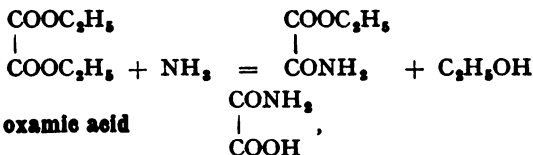


On continued boiling with alcoholic potash, the second ester grouping is hydrolysed, yielding potassium oxalate. The free monoalkyl esters of oxalic acids, such as **ethyl hydrogen oxalate** $\text{HO.CO.CO.OC}_2\text{H}_5$, are acid liquids, which are rapidly hydrolysed on addition of water.

Ethyl oxalate, on treatment with ammonia, yields **ethyl oxamate**



which is both an ester and an amide :



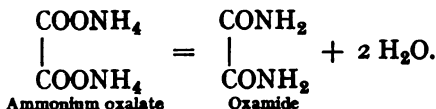
The free **oxamic acid**

and some of its metallic salts, are also known.

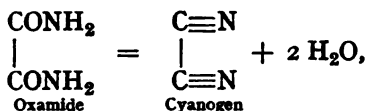
Oxamide



is formed, in the usual manner, by heating ammonium oxalate :

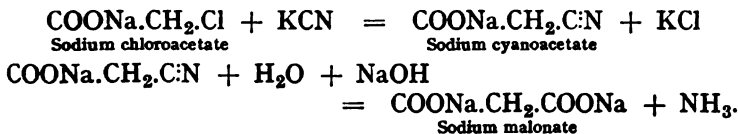


On heating alone, or with dehydrating agents such as phosphorus pentoxide, it yields cyanogen :

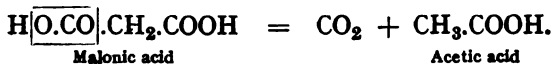


which may thus be regarded as the nitrile derived from oxalic acid.

Malonic acid $\text{COOH}\cdot\text{CH}_2\cdot\text{COOH}$ was first obtained by the oxidation of malic acid (p. 247). It is synthetically prepared from monochloroacetic acid, by causing this to react with potassium cyanide, and hydrolysing the resulting cyanoacetic acid :



Malonic acid is a white crystalline solid which melts at 133° and is extremely soluble in water. It decomposes on heating to slightly above its melting-point, yielding carbon dioxide and acetic acid :

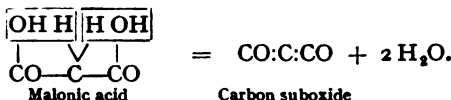


All homologues of malonic acid in which both carboxyl groups are attached to the same carbon atom undergo this decomposition on heating.

Malonyl chloride $\text{Cl.CO.CH}_2\text{.COCl}$,
and **malonamide** $\text{NH}_2\text{.CO.CH}_2\text{.CO.NH}_2$,

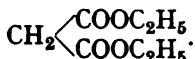
are known, but call for no mention beyond that of their existence.

On heating malonic acid or ethyl malonate with phosphorus pentoxide, **carbon suboxide** C_3O_2 is produced. It bears to malonic acid the same relation that keten (p. 172) bears to acetic acid :



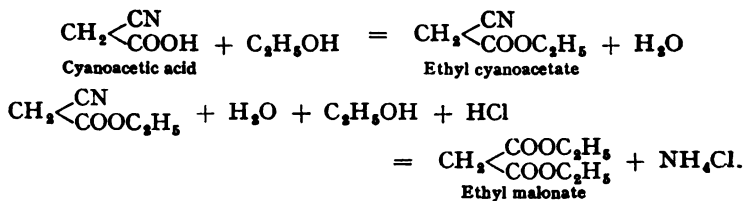
It is a gas of irritating odour, which may be condensed to a liquid boiling at 7° . Its chemical behaviour is that of a true keten : for instance, it reacts at once with water, regenerating malonic acid.

Of the malonic esters, the most important is **ethyl malonate**

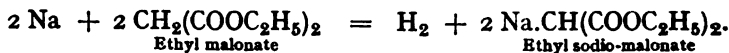


This is a pleasant-smelling oil, insoluble in water, which boils at 198° .

It may be prepared in the ordinary way from ethyl alcohol and malonic acid, or directly from cyanoacetic acid by warming this substance with alcohol in presence of a small quantity of concentrated sulphuric acid or hydrogen chloride :

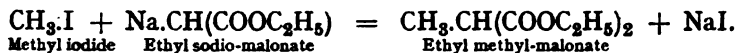


The principal feature of interest in malonic esters is the ease with which the hydrogen atoms in the methylene ($>\text{CH}_2$) group can be replaced. If sodium be added to malonic ester, hydrogen is evolved, and a sodium derivative of malonic ester is formed :

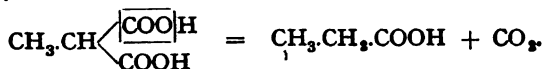


This sodium compound can be dissolved unchanged in absolute

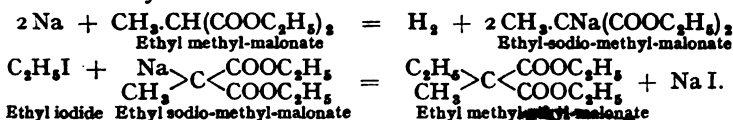
alcohol; on treatment with alkyl halides a double decomposition takes place :



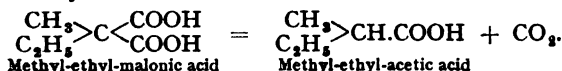
By this reaction, any homologue of malonic ester can be prepared, by selecting the suitable alkyl halide. If the resulting ester be hydrolysed, and the free acid heated above its melting-point, the corresponding monocarboxylic acid is produced by loss of carbon dioxide :



The second hydrogen atom in malonic ester may be replaced in the same way :

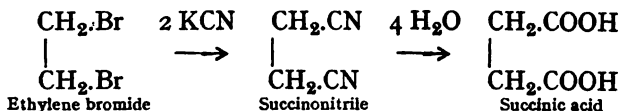


On hydrolysis, the free acid can be obtained, which on heating loses carbon dioxide in like manner, forming the corresponding monocarboxylic acid :

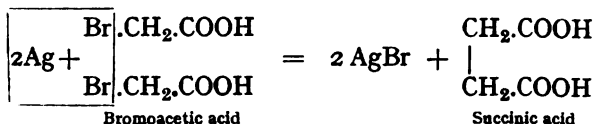


Ethyl malonate has, on account of this useful property, been the starting substance of many syntheses.

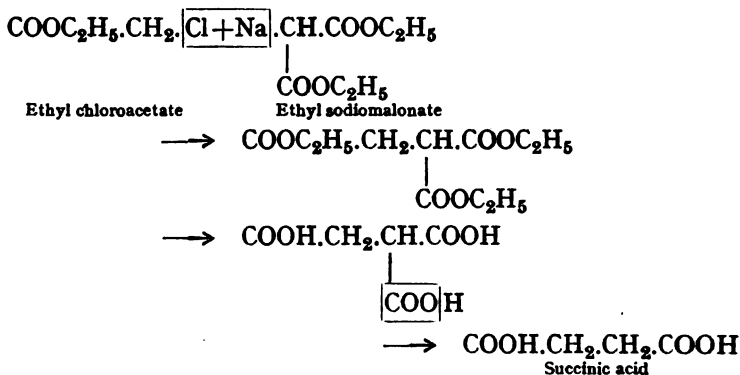
Succinic acid $\text{COOH}.\text{CH}_2.\text{CH}_2.\text{COOH}$ was first obtained by distilling amber (*succinum*). It can be synthetically prepared from ethylene bromide and potassium cyanide :



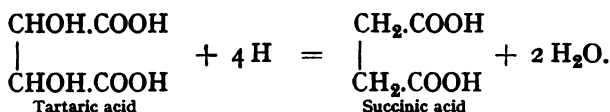
by general methods. It may also be obtained in small yield by heating bromoacetic acid with finely divided silver :



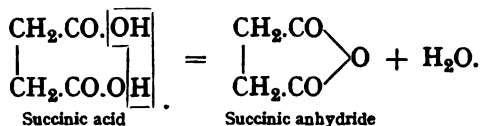
Another method of preparation, which also illustrates the use of malonic ester, is the following :



In technical practice it is usually manufactured by fermentation of ammonium tartrate (p. 249), whereby the tartaric acid is reduced to succinic acid. This reduction may also be effected by heating with hydriodic acid :

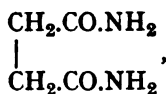


Succinic acid is a white crystalline solid which melts at 182° . On heating alone, or with a dehydrating agent, it is converted into **succinic anhydride**, a solid melting at 120° :

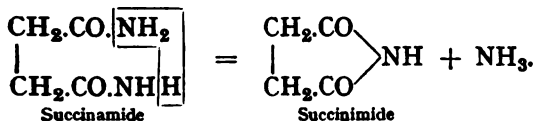


The readiness which succinic acid displays in the formation of an anhydride is an example of the general tendency of organic compounds to form, whenever possible, such *cyclic* systems containing either five or six members in the ring.

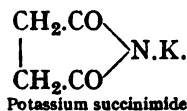
The same is observed with **succinamide**



which is produced by the action of ammonia on esters of succinic acid. Succinamide, on heating, loses ammonia and passes into **succinimide** :



Succinimide is of interest in that it possesses weakly acid properties and can yield salts such as :



It will be recalled that acid amides in which one amino ($-\text{NH}_2$) group is attached to one carbonyl group ($-\text{CO.NH}_2$), are neutral bodies. Carbamide, in which two amino groups are attached to one carbonyl group ($\text{NH}_2\text{CO.NH}_2$), possesses weakly basic properties ; on the other hand, succinimide, in which one nitrogen atom is placed between two carbonyl groups, functions as an acid. Here we see again the effects of mutual influence between carbonyl and amino groups.

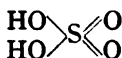
CHAPTER XII

ESTERS OF INORGANIC ACIDS

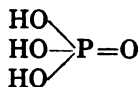
ESTERS of inorganic acids bear the same relation to salts of inorganic acids as esters of carboxylic acids do to salts of carboxylic acids. All inorganic acids, with the exception of a few, such as hydrochloric acid, consist of hydroxyl groups united to "non-metallic" atoms or complexes. Such are :



Nitric acid



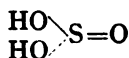
Sulphuric acid



Orthophosphoric acid



Nitrous acid



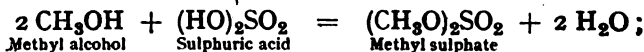
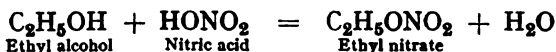
Sulphurous acid



Orthophosphorous acid

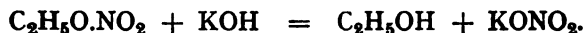
In esters of these acids the hydroxylic hydrogen atoms are replaced by alkyl groups. In fact, halogen-substituted hydrocarbons themselves may be regarded as alkyl halides, or esters of hydrochloric, hydrobromic, or hydriodic acids, though for the sake of simplicity they have been treated as a class for themselves.

Esters of inorganic acids may be prepared by the general methods which lead to the formation of carboxylic esters ; either by direct interaction of acids and alcohols :

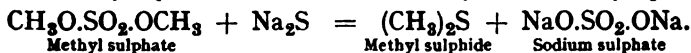
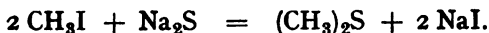


$$\begin{array}{ccccccc} 3 \text{ C}_2\text{H}_5\text{ONa} & + & \text{POCl}_3 & = & (\text{C}_2\text{H}_5\text{O})_3\text{PO} & + & 3 \text{ NaCl} ; \\ \text{Sodium ethoxide} & & \text{Phosphoryl chloride} & & \text{Ethyl phosphate} & & \end{array}$$
$$3 \text{ CH}_3\text{I} + (\text{AgO})_3\text{PO} = (\text{CH}_3\text{O})_3\text{PO} + 3 \text{ AgI}.$$

In chemical behaviour, the esters of inorganic acids resemble the alkyl halides ; on treatment with alkali they are hydrolysed, yielding the alcohols :


$$\text{CH}_3\text{O.SO}_2.\text{OCH}_3 + \text{NH}_3 = \text{CH}_3.\text{NH}_3\text{O.SO}_2.\text{OCH}_3$$

Methyl sulphate Methylammonium methylsulphate


$$\text{CH}_3\text{I} + \text{NH}_2 = \text{CH}_3.\text{NH}_2.\text{I}$$

$$2 \text{C}_2\text{H}_5\text{O}.\text{SO}_2.\text{OK} + \text{K}_2\text{S} = (\text{C}_2\text{H}_5)_2\text{S} + 2 \text{K}_2\text{SO}_4.$$

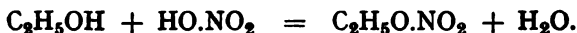
Potassium ethylsulphate Ethyl sulphide

$$\text{C}_2\text{H}_5\text{O.SO}_3.\text{OK} + \text{KOH} = \text{C}_2\text{H}_5\text{OH} + \text{K}_2\text{SO}_4.$$

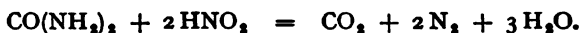
The completely esterified acids, or normal esters, such as $(\text{CH}_3\text{O})_2\text{SO}_2$, are neutral oils, which are insoluble in

water. The partly esterified acids, such as the alkylsulphuric acids $\text{RO.SO}_2\text{OH}$, and their salts, are soluble in water.

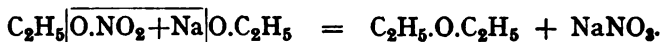
Alkyl nitrates RO.NO_2 are formed by the action of concentrated nitric acid upon alcohols :



In practice, if alcohols be mixed with concentrated nitric acid, violent oxidation soon sets in; the mixture becomes hot, and oxides of nitrogen are copiously evolved. The oxidation is due to the presence at the outset of small quantities of nitrous acid in the nitric acid; this can be avoided by the addition of carbamide nitrate (p. 181), which reacts with the nitrous acid in the sense of the equation :



The alkyl nitrates are colourless liquids, which are insoluble in water. They react with metallic alkoxides, yielding ethers :



They may be reduced with tin and hydrochloric acid, the corresponding alcohol and hydroxylamine being produced :

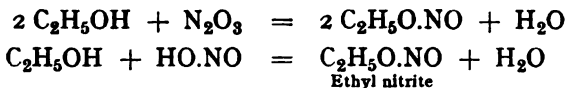


Methyl nitrate boils at 66° , **ethyl nitrate** boils at 87° .

On rapid heating, alkyl nitrates are prone to decompose with explosive violence. This instability is most marked in the trinitrate of glycerol, or **glyceryl trinitrate** (p. 132). This is prepared by treating glycerol with a well-cooled mixture of fuming nitric acid and concentrated sulphuric acid, esterification taking place, as shown on p. 132. The mixture, after standing for some time, is run into water, from which the ester separates as a heavy oil, which is then washed with water and dilute sodium carbonate to remove free acid, and finally dried by filtration through felt. Glyceryl trinitrate, which is technically known as *nitroglycerine*, is employed as a high explosive, since it decomposes with terrific violence when detonated. "Dynamite," which is a mixture of nitroglycerine and a porous diatomaceous earth called Kieselguhr, is safer to handle, since it is less liable to uncertain and unintended explosion.

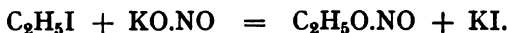
Cellulose (p. 285) may be converted into its nitric esters in the same way, the products being known as "gun-cotton," "pyroxylin," etc. A description of these esters will be given later (p. 287). Mixtures of nitroglycerine and gun-cotton are employed in the manufacture of the well-known explosives "blasting gelatine," "cordite," etc.

Alkyl nitrites RO.NO may be prepared by the direct action of nitrous anhydride (N_2O_3) or nitrous acid upon alcohols :



A better method is gradually to add a solution of sulphuric acid in alcohol to a concentrated solution of sodium nitrite, whereby the nitrous acid liberated by the sulphuric acid at once reacts with the alcohol.

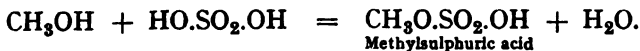
They may also be prepared by the interaction of alkyl halides with sodium or potassium nitrite :



The alkyl nitrites are insoluble in water, and possess lower boiling-points than the corresponding nitrates. They have powerful physiological action, lowering the blood pressure when their vapour is inhaled, thus accelerating the action of the heart.

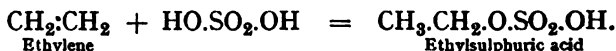
Methyl nitrite $\text{CH}_3\text{O.NO}$ is a gas at ordinary temperature, boiling at -12° . **Ethyl nitrite** $\text{C}_2\text{H}_5\text{O.NO}$ boils at 17° . A solution in ethyl alcohol, known as "sweet spirits of nitre," is employed medicinally. **Isoamyl nitrite** $(\text{CH}_3)_2\text{CH.CH}_2\text{CH}_2\text{O.NO}$ boils at 94° – 95° . It affords instant relief in cases of *angina pectoris*.

Alkylsulphuric acids $\text{RO.SO}_2\text{OH}$ may be regarded as sulphuric acid in which one of the hydrogen atoms is replaced by an alkyl radicle. They are formed on warming alcohols with concentrated sulphuric acid :

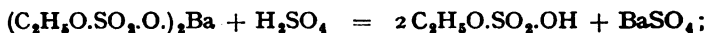


Those containing two or more carbon atoms in the alkyl radicle

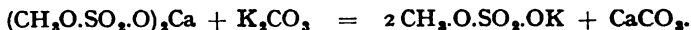
can also be prepared by passing ethylenic hydrocarbons into concentrated sulphuric acid :



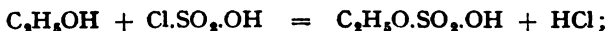
The alkylsulphuric acids may be separated from the excess of sulphuric acid by adding water and an excess of calcium carbonate, barium carbonate, or lead carbonate, and filtering. The filtrate contains the soluble metallic salt of the alkylsulphuric acid, the insoluble metallic sulphate remaining on the filter. The free acid may be obtained by adding the requisite quantity of sulphuric acid and again filtering :



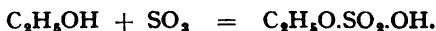
whilst the alkali salts may be produced by decomposing the calcium salt with alkali carbonate :



Other methods of preparation consist in gradually adding alcohols to well-cooled chlorosulphonic acid :



and in passing the vapour of sulphuric anhydride into the well-cooled alcohol :

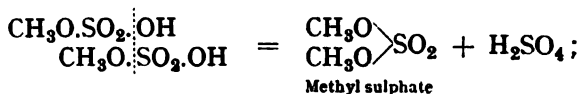


The free acids are hygroscopic syrups, which cannot be distilled without decomposition. The salts are stable crystalline solids, which dissolve readily in water. Their dilute aqueous solutions may be heated without appreciable hydrolysis taking place ; on addition of alkali, the alcohols and metallic sulphates are produced on boiling :

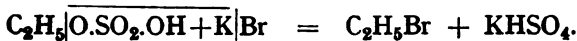


The alkylating action of alkylsulphates has already been discussed (p. 193).

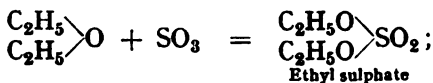
On heating the free acid, decomposition takes place. Methylsulphuric acid breaks down into sulphuric acid and methyl sulphate :



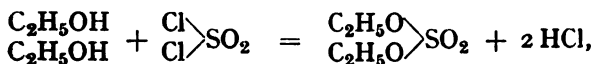
whilst ethylsulphuric acid yields ethylene and sulphuric acid (cf. p. 84). On heating with alcohols they yield ethers (p. 136); on heating with metallic halides, alkyl halides are produced:



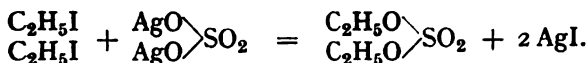
Alkyl sulphates $(\text{RO})_2\text{SO}_2$, are formed by adding sulphuric anhydride to ethers:



also by the action of sulphuryl chloride on sufficient alcohol:

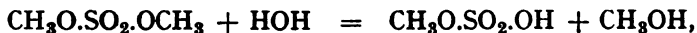


and by interaction of alkyl halides with silver sulphate:

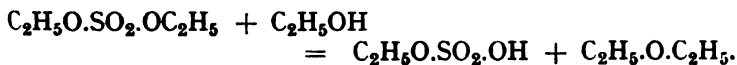


The formation of methyl sulphate by heating methylsulphuric acid has just been mentioned.

They are heavy liquids, insoluble in water. On prolonged boiling with water, they are hydrolysed in the sense of the equation:



and by alcohols in an analogous manner:



Their vapours are poisonous when inhaled.

Methyl sulphate $(\text{CH}_3\text{O})_2\text{SO}_2$ boils at 187° . It is manufactured by distilling ethylsulphuric acid under reduced pressure, and finds wide application in technical and laboratory practice as a methylating agent. **Ethyl sulphate** $(\text{C}_2\text{H}_5\text{O})_2\text{SO}_2$ boils at 208° .

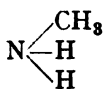
CHAPTER XIII

AMINES

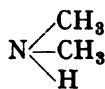
THE name *amine* is a wide term, applied to all derivatives of ammonia in which either one, two, or three of the hydrogen atoms in the ammonia molecule are replaced by alkyl groups. For example, on replacing the hydrogen atom by methyl groups we have :



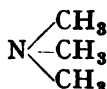
Ammonia



Methylamine



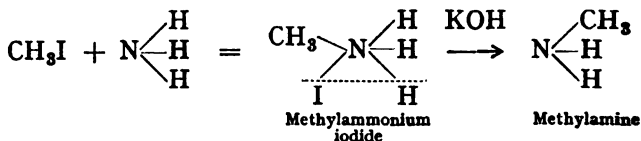
Dimethylamine



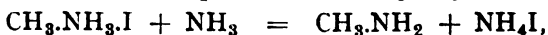
Trimethylamine

Methylamine and similar mono-alkyl derivatives of ammonia are termed *primary amines*; dimethylamine is a *secondary amine*; trimethylamine a *tertiary amine*. The radicle —NH_2 is termed an *amino* group, the radicle >NH is termed an *imino* group, while the nitrogen atom in tertiary amines >N is usually called a "tertiary nitrogen atom."

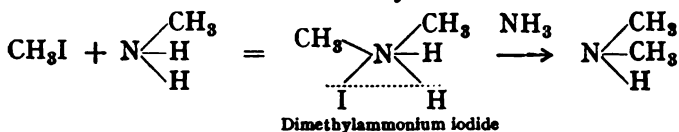
Alkylamines may be obtained by the interaction of alkyl halides and ammonia, subsequently decomposing the alkylammonium halide with alkali :



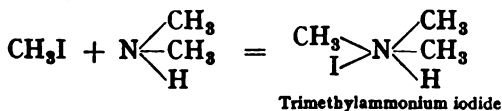
This reaction, however, does not proceed as simply as the equation would indicate. Some of the alkylammonium iodide reacts with the ammonia present, liberating alkylamine :



and this in turn reacts with more alkyl halide :

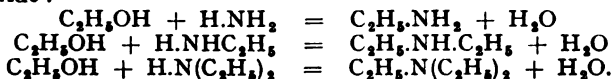


This process repeats itself, with formation of trialkylammonium halide :



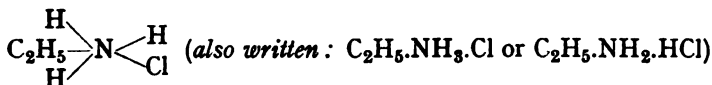
so that, on rendering the final reaction-product alkaline and distilling, a mixture of ammonia and primary, secondary, and tertiary amines is obtained.

A similar mixture of primary, secondary and tertiary amines is produced by heating alcohols with ammonia in presence of zinc chloride :



The separation of primary, secondary, and tertiary amines is a matter of some difficulty, and will be discussed later.

All these alkyl amines are strong bases, which form alkyl ammonium salts with acids :

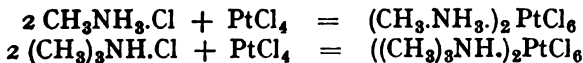


Ethylammonium chloride, also called Ethylamine hydrochloride

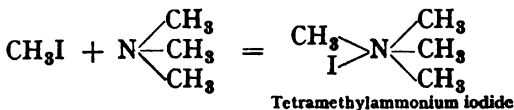
They can also form more complex salts ; for instance, with hydrogen platinichloride. On adding platinic chloride to a solution of ammonium chloride, ammonium platinichloride, as is well known, is produced :



Platinichlorides are produced in the same way from solutions of alkyl amines in hydrochloric acid :



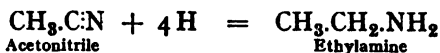
On treating a tertiary amine with an alkyl halide, addition takes place, yielding a **tetra-alkylammonium halide**:



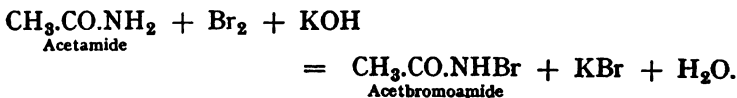
Such compounds, known by the general term **quaternary ammonium salts**, are not decomposed by alkali.

Primary amines may be prepared by general methods, which do not lead to the simultaneous formation of secondary and tertiary amines.

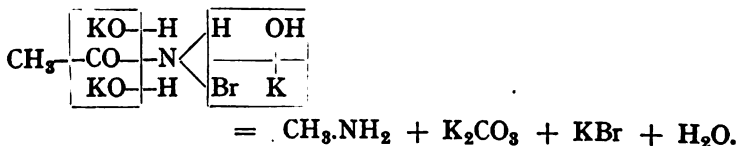
Nitriles (p. 221) on reduction, yield primary amines :



Acid amides can be converted into primary amines containing one carbon atom less in the molecule, by a peculiar reaction discovered by Hofmann ; on treating an amide with bromine and caustic alkali, one of the hydrogen atoms in the amino ($-\text{NH}_2$) group is replaced by bromine :



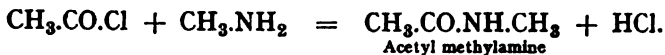
On boiling an alkaline solution of the bromoamide, carbon dioxide and hydrogen bromide is split off, and the primary amine is set free :



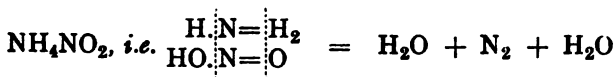
Finally, primary amines are produced by the hydrolysis of alkyl isocyanates (p. 228) :



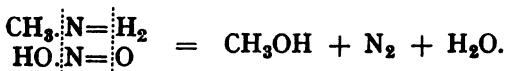
The properties of primary amines closely resemble those of ammonia. Acid chlorides or acid anhydrides react with them just as they do with ammonia, to form acyl derivatives of amines (*substituted amides*), a hydrogen atom being replaced by an acid radicle :



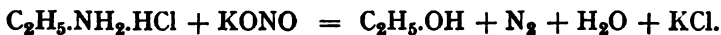
The decomposition of ammonium nitrite by heat :



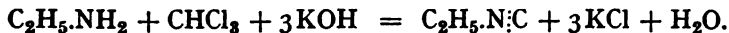
is paralleled by the action of nitrous acid upon primary amines, alcohols being produced :



In carrying out this reaction, it is customary to add sodium nitrite to a solution of a primary alkylammonium salt :



A reaction characteristic of primary amines is the formation of *isocyanides* (isonitriles or carbylamines) on warming with chloroform and alcoholic potash :

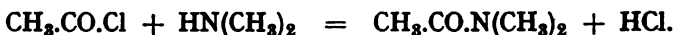


Isocyanides have a powerful and disagreeable odour, so that this reaction can be employed as a test for primary amines and for chloroform. It is known as the *carbylamine* reaction.

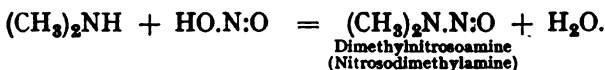
Secondary amines can be prepared by the action of alkyl halides, or alkyl esters of some inorganic acids, such, for instance, as potassium methylsulphate $\text{CH}_3\text{O.SO}_2\text{OK}$, upon primary amines (p. 22). By this means it is possible to obtain secondary amines containing two different alkyl radicles, as, for instance, methyl-ethylamine $\text{CH}_3\text{NH.C}_2\text{H}_5$.

Secondary amines, which, like primary amines, contain a

hydrogen atom attached to the nitrogen atom, react with acid chlorides and anhydrides to form *acyl* derivatives :

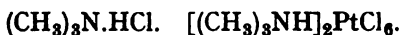


Their behaviour towards nitrous acid differs from that of ammonia and primary amines, since only one hydrogen atom is available for attack. In this case a *nitroso* derivative (*nitrosoamine*) is formed :



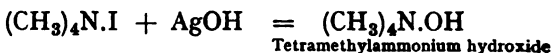
These nitrosoamines, which may be regarded as acyl derivatives of secondary amines in which the acyl group is the acid radicle of nitrous acid (—N:O), are for the most part yellow oils with neutral or only weakly basic properties.

Tertiary amines can be prepared by heating secondary amines with alkyl halides and decomposing the product with alkali (p. 22). They resemble ammonia and primary and secondary amines in that they are volatile, and form salts with simple and complex acids, *e.g.*



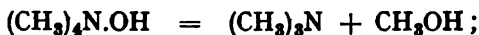
Owing to the absence of hydrogen atoms directly united to the nitrogen atoms, they form no acyl derivatives on treatment with acid anhydrides and nitrous acid.

On treatment with alkyl halides they yield **quaternary ammonium halides**. These are ammonium salts in which all the hydrogen atoms are replaced by alkyl groups (p. 22); for this reason no hydrogen halide is split off on treatment with alkali. On treatment in aqueous solution with silver oxide, silver iodide is formed, and a quaternary ammonium hydroxide remains in solution :

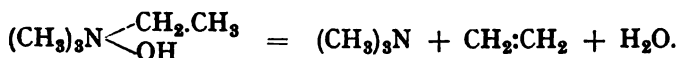


If a solution of such a quaternary ammonium hydroxide be evaporated, the hydroxide remains as a solid, which,

however, decomposes on further heating. Tetramethylammonium hydroxide thus breaks down with trimethylamine and methyl alcohol :



whilst quaternary ammonium hydroxides in which one of the alkyl groups contains more than one carbon atom yield tertiary amines and ethylenic hydrocarbons. Thus trimethylethylammonium hydroxide yields trimethylamine, ethylene, and water :



Quaternary ammonium hydroxides are powerful bases, being dissociated in aqueous solution to an even greater degree than the hydroxides of the alkali metals.

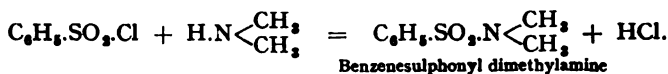
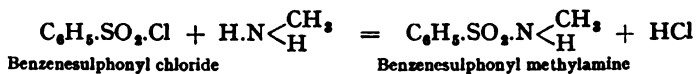
SEPARATION OF PRIMARY, SECONDARY, AND TERTIARY AMINES

From what has already been stated, primary, secondary, and tertiary amines may be distinguished by the behaviour towards nitrous acid ; primary amines at once yield elemental nitrogen and an alcohol ; secondary bases are converted into nitroso derivatives ; while tertiary amines are unaltered. This process can, however, not well be applied for their separation, for the reconversion of nitrosoamines into secondary amines is troublesome, and primary amines are thus irrecoverably decomposed.

Primary and secondary amines may be removed from such a mixture by heating with acetic anhydride, whereby neutral acetyl derivatives are formed, the basic tertiary amine being left unchanged. The separation of these acetyl derivatives from each other is, however, a matter of considerable difficulty.

Recourse must therefore be had to a substance, to be described later (p. 333), termed *benzenesulphonyl chloride*. This is the chloride of a sulphonic acid (p. 332), and possesses the formula

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. It reacts with primary and secondary amines after the manner of all acid chlorides :

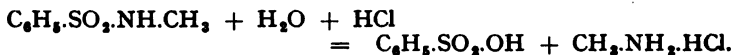


Tertiary amines are unaffected by this reagent.

The products are water-insoluble derivatives of *benzenesulphonamide* (p. 334) $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$; those which contain a hydrogen atom attached to nitrogen, as in $\text{C}_6\text{H}_5\text{SO}_2\text{NH}\cdot\text{CH}_3$, are capable of forming water-soluble sodium salts, such as $\text{C}_6\text{H}_5\text{SO}_2\text{N} \begin{smallmatrix} \text{CH}_3 \\ \text{Na} \end{smallmatrix}$, on treatment with sodium hydroxide solution.

The benzenesulphonyl derivatives of secondary amines, which contain no hydrogen atom attached to nitrogen, remain insoluble in caustic soda, and can thus be separated.

On heating these benzenesulphonyl derivatives with hydrochloric acid they are hydrolysed, and the pure primary and secondary amines can be recovered by treatment with alkali :



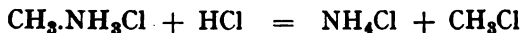
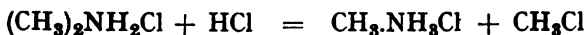
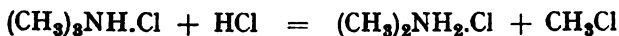
INDIVIDUAL AMINES

Methylamine CH_3NH_2 , **dimethylamine** $(\text{CH}_3)_2\text{NH}$, and **trimethylamine** $(\text{CH}_3)_3\text{N}$ are gases under ordinary atmospheric conditions. They are strong bases, like ammonia, and possess powerful ammoniacal odours. All are extremely soluble in water. The formation of methylamine by reduction of hydrogen cyanide is worthy of note :



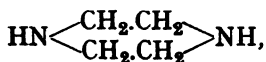
Dimethylamine and trimethylamine form the chief constituents of the amines occurring in herring brine, and in the residues of the sugar-beet juices (p. 283).

The methylamines are employed in technical practice chiefly for the preparation of methyl chloride, by heating their hydrochlorides in a current of hydrogen chloride (p. 98) :

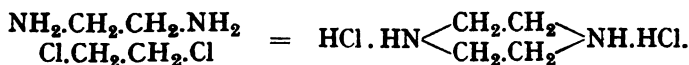
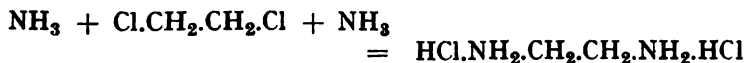


Ethylamine $\text{CH}_3.\text{CH}_2.\text{NH}_2$ is a liquid boiling at 19° , possessing properties similar to those of methylamine. The higher members have higher boiling points, and their solubility in water decreases on ascending the scale.

Amines containing more than one amino group in the molecule are also known. Examples of these are **ethylenediamine** $\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$, and **piperazine** (diethylenediamine)



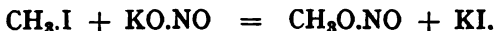
prepared from ethylene chloride or bromide and ammonia :



CHAPTER XIV

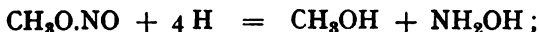
NITROPARAFFINS

IN a previous chapter (p. 195) it was stated that alkyl nitrites could be produced by the action of alkyl halides upon sodium or potassium nitrite :

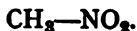


If, on the other hand, silver nitrite be treated with methyl iodide, a vigorous reaction takes place, and a liquid is formed which boils at 101° . Analysis shows this liquid to possess the composition $\text{CH}_3\text{O}_2\text{N}$, and molecular weight determination leads to the simple formula $\text{CH}_3\text{O}_2\text{N}$. The product is therefore isomeric with the methyl nitrite. Identity of the two substances is out of the question, as methyl nitrite boils at -12° , or 113° lower than this isomer.

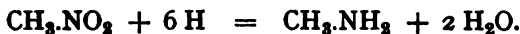
A constitutional difference between the two is shown by their behaviour towards reducing agents. Methyl nitrite, when reduced, is converted into methyl alcohol and hydroxylamine :



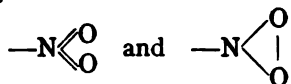
this new product, on the other hand, yields methylamine CH_3NH_2 on reduction. From this fact we must conclude that the nitrogen atom is directly attached to the carbon atom. Assuming—and in view of other reactions involving methyl iodide the assumption is a legitimate one—that the methyl group remains intact throughout the reactions, we have no alternative but to formulate the constitution of the substance as :



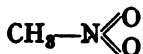
The reduction would thus take place in the sense of :



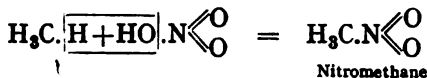
There are two possible ways in which the group —NO_2 may be formulated, namely :



In inorganic chemistry we have been accustomed to apply the grouping —O—O— only to strong oxidising agents, such as hydrogen peroxide ; the new product CH_3NO_2 possesses very weak oxidising properties, so that the formulation :



is therefore adopted. This is supported by the formation of small quantities of this liquid, to which the name **nitromethane** has been given, by the action of nitric acid upon methane :

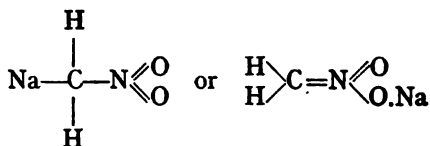


On treating silver nitrite with ethyl iodide, a small quantity of ethyl nitrite is formed, together with a greater amount of a liquid $\text{C}_2\text{H}_5\text{O}_2\text{N}$, which, from its properties, is obviously a homologue of nitromethane, and must be regarded as **nitroethane** $\text{C}_2\text{H}_5\text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, since on reduction it yields ethylamine $\text{C}_2\text{H}_5\text{NH}_2$. It boils at 113° , and is likewise produced in small quantities by the interaction of nitric acid with ethane.

When silver nitrite is treated with alkyl iodides of increasing molecular weight, the proportion of alkyl nitrite formed becomes greater at the expense of nitroparaffin.

The most interesting property of nitroparaffins is that of forming metallic salts. Nitromethane is insoluble in water, but dissolves in aqueous alkali. On treatment with alcoholic sodium ethoxide it yields a white crystalline precipitate, which

on analysis is found to have the composition $\text{CH}_2\text{O}_2\text{NNa}$. This may be formulated either as :



Sodium nitromethane

The second formula has, for a variety of reasons, been adopted.



can form a sodium salt $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_3 \end{array} \text{C} = \text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{ONa} \end{array}$

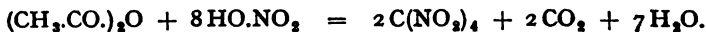


is unable to yield metallic derivatives.

In addition to these mononitroderivatives, nitroparaffins containing more than one nitro group are known. In methane all the hydrogen atoms may be successively replaced by nitro groups, just as they may be by chlorine or bromine atoms, giving the series :



The most important of these substances is **tetranitromethane**, which is produced by the prolonged action of fuming nitric acid upon acetic anhydride in the cold, carbon dioxide being simultaneously evolved :



It is a colourless substance which melts at 13° and boils at 126° .

CHAPTER XV

ORGANIC COMPOUNDS OF SULPHUR

IN works on inorganic chemistry, points of similarity between oxygen and sulphur have been made amply clear by noting, for example, the features of resemblance and difference between water and hydrogen sulphide. These points may be extended into the domain of organic chemistry.

Just as alcohols and ethers may be regarded as mono- and di-alkyl substitution-products of water :



so do we obtain, by replacing the oxygen by sulphur, mono- and di-alkyl derivatives of hydrogen sulphide. These are known as alkyl hydrosulphides (or mercaptans), and alkyl sulphides, respectively :



Hydrosulphides



Sulphides

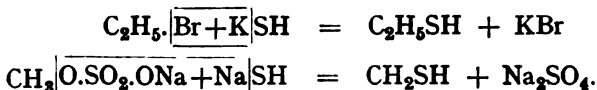
The chief points wherein bivalent sulphur differs from oxygen are : firstly, the faintly acidic nature and instability towards oxidising agents of its hydride (hydrogen sulphide) ; secondly, a tendency for two or more atoms to unite directly, as in polysulphides ; thirdly, a marked tendency to assume a higher valency. Most of these features are not entirely absent in oxygen ; they are merely less fully developed.

ALKYL HYDROSULPHIDES or MERCAPTANS

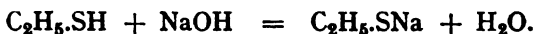
R.SH are the thio analogues of the alcohols. The chief method of preparation is by the action of alkylating agents,

P

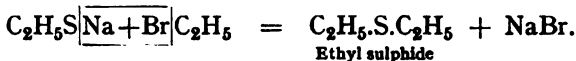
such as alkyl halides or esters of inorganic acids, upon alkali hydrosulphides :



Methyl hydrosulphide CH_3SH boils at 6° ; **ethyl hydrosulphide** $\text{C}_2\text{H}_5\text{SH}$ boils at 37° . Mercaptans are insoluble in water and possess powerful and disagreeable odours. They behave as hydrogen sulphide in which one of the hydrogen atoms is replaced by an alkyl group, in that the remaining hydrogen atom is readily replaceable by metals : they dissolve in aqueous alkalis, yielding solutions of the alkali salts (usually called *mercaptides*) :

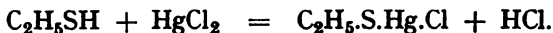


The metallic atom in mercaptides can readily be exchanged for an alkyl group by treatment with alkyl halides, *alkyl sulphides* being formed :



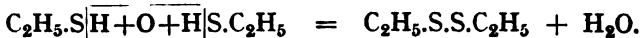
In structure these alkyl sulphides resemble the ethers ; they are hence sometimes termed *thioethers*.

Characteristic of mercaptans is their property of reacting with mercuric salts, forming compounds of mercury :

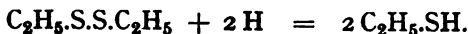


These mercury derivatives are for the most part crystalline solids, insoluble in water. The generic name for alkyl hydrosulphides is derived from this property, *corpus mercurio aptum* (a body having affinity for mercury) being contracted to *mercaptan*.

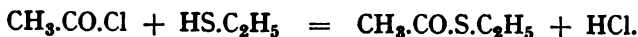
The hydrogen atom attached to the sulphur atom in hydrosulphides—like that in hydrogen sulphide—is readily removed by oxidation, yielding **alkyl disulphides** :



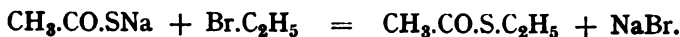
Alkyl disulphides, on reduction, are readily reconverted into hydrosulphides :



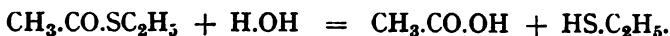
Alkyl hydrosulphides, like alcohols, may be esterified. Thus on treatment with acetyl chloride they yield esters of **thioacetic acid** $\text{CH}_3.\text{CO.SH}$:



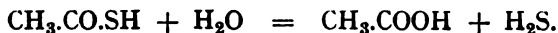
The same products may be obtained by treating alkali metallic thioacetates with alkyl halides :



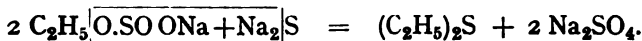
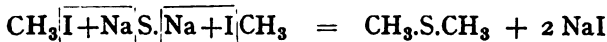
These esters may be hydrolysed, yielding mercaptan and acetic acid :



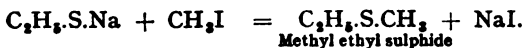
Thioacetic acid is known in the free state ; on boiling with water or dilute acids or alkalis, it is hydrolysed, yielding acetic acid and hydrogen sulphide :



ALKYL SULPHIDES R.S.R may be prepared by the action of alkyl halides or esters of inorganic esters upon sulphides of alkali metals :



"Mixed" sulphides, in which the sulphur atom is united to two different alkyl groups, are produced by treating a mercaptide with a halide of a different alkyl radicle :



Methyl ethyl sulphide

Alkyl sulphides are colourless liquids, which are insoluble in water and possess unpleasant and penetrating odours. Like ethers, they are stable substances, and do not react with alkalis or even metallic sodium. **Methyl sulphide** $(\text{CH}_3)_2\text{S}$ boils

at 38°, **ethyl sulphide** $(C_2H_5)_2S$ at 92°. **Allyl sulphide** $(CH_2:CH.CH_2)_2S$ boils at 140°.

In this connection, mention should be made of **allyl disulphide**



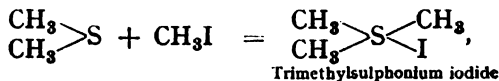
the odorous principle in the garlic plant (*Allium sativum*). The name *allyl* is derived from *allium*.

As above mentioned, bivalent sulphur displays a strong tendency to pass into higher-valent conditions. Thus with mercuric chloride addition-products $R_2S.HgCl_2$ are at once formed, the majority of these being crystalline solids. From their chemical character it is customary to formulate them as containing quadrivalent sulphur :

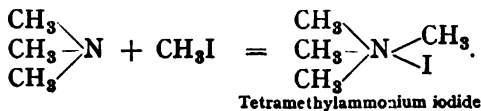


Again, on bringing alkyl halides and alkyl sulphides together, addition products are formed. Thus on treating methyl sulphide with methyl iodide, a white crystalline solid is produced with evolution of heat, the composition of which corresponds with the formula $(CH_3)_3S.CH_3I$. These compounds cannot, however, be regarded as loose "molecular" addition-products, because they are stable, and their aqueous solutions (although both components were insoluble in water, the product is soluble) conduct an electric current. The halogen is immediately and completely precipitated by silver nitrate; further, on treatment with silver oxide and water, they yield bases as strong as potassium hydroxide.

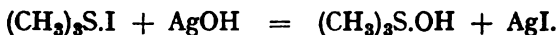
These facts point to a close analogy with quaternary ammonium salts, and there can be no doubt that such compounds must be derivatives of quadrivalent sulphur :



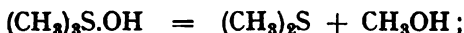
analogous to :



They are termed **sulphonium** salts, the free bases being the sulphonium hydroxides :



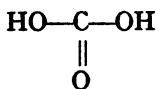
They likewise resemble the quaternary ammonium compounds in the decomposition of their hydroxides. Trimethylsulphonium hydroxide, on heating, breaks up into methyl sulphide and methyl alcohol (cf. p. 203) :



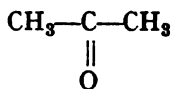
while those in which at least one alkyl group contains more than one carbon atom decompose into alkyl sulphide, an ethylenic hydrocarbon, and water (cf. p. 81).

In addition to the above-described ways in which bivalent sulphur is converted into the quadrivalent condition, there is another general manner, that of oxidation.

It will be recalled that ketones are compounds which may theoretically be derived by replacing the two hydroxyl groups in the hypothetical hydrated carbonic acid by alkyl groups :

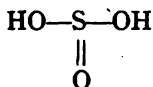


Carbonic acid

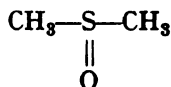


Dimethyl ketone

an analogous series of compounds may be imagined as being thus derived from sulphurous acid. These are the **sulphoxides**, obtained by gentle oxidation of sulphides :



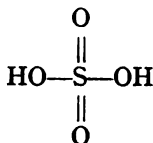
Sulphurous acid



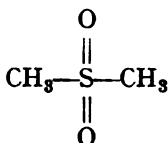
Dimethyl sulphoxide

They are neutral or slightly basic compounds of only theoretical importance. On further oxidation they pass into the **sulphones**, which are compounds bearing a similar relation to

sulphuric acid, in which the sulphur functions as a sexavalent atom :



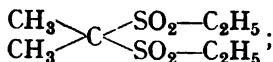
Sulphuric acid



Dimethyl sulphone

Sulphones are characterised by great stability ; they resist the action of oxidising or reducing agents.

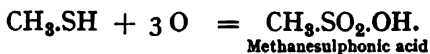
Methyl sulphone $\text{CH}_3.\text{SO}_2.\text{CH}_3$ melts at 109° ; **ethyl sulphone** $\text{C}_2\text{H}_5.\text{SO}_2.\text{C}_2\text{H}_5$ melts at 70° . **Sulphonal** is a compound containing two sulphonyl ($>\text{SO}_2$) groups :



it melts at 125° , and is employed in medicine as a soporific.

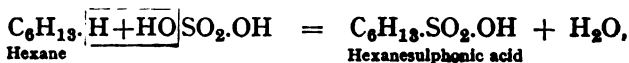
To turn now to the oxidation products of mercaptans : mild oxidation—by means of iodine or ferric chloride—leads to alkyl disulphides (p. 219) ; on more vigorous oxidation the sulphur atom unites with oxygen, yielding acid substances. There are two series of such acids : **sulphinic acids** $\text{R}.\text{SO}.\text{OH}$, corresponding with sulphurous acid and sulfoxides, containing quadrivalent sulphur ; and **sulphonic acids** $\text{R}.\text{SO}_2.\text{OH}$, corresponding with sulphuric acid and sulphones, containing sexavalent sulphur.

The sulphinic acids call for no mention beyond that of their existence ; the sulphonic acids are produced by violent oxidation—for example, by means of concentrated nitric acid—of alkyl hydrosulphides :



Methanesulphonic acid

They are also formed in minute quantities by the action of fuming sulphuric acid upon some paraffin hydrocarbons :



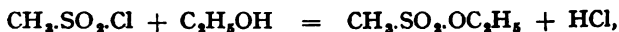
Hexane

Hexanesulphonic acid

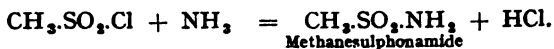
Sulphonic acids are very strong acids, soluble in water; they cannot be distilled without decomposition. In some respects they resemble carboxylic acids; on treatment with phosphorus pentachloride they yield **sulphonic chlorides** :



which react with alcohols forming **sulphonic esters** :



and with ammonia, to form **sulphonic amides** :



In their chemical behaviour, these esters resemble esters of inorganic acids rather than carboxylic esters. The amides have distinctly acid properties (cf. p. 334).

Sulphonic acids, like sulphones, are not attacked by oxidising and reducing agents.

CHAPTER XVI

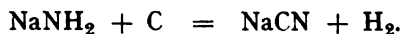
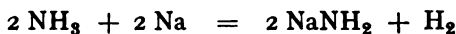
CYANOGEN COMPOUNDS

CYANIDES

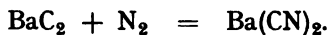
METALLIC cyanides, such as potassium cyanide, $\text{K.C}\equiv\text{N}$, are produced by strongly heating carbon and a basic substance, such as potassium carbonate, in an atmosphere of nitrogen :



Sodium cyanide is formed by heating sodium in a current of ammonia and subsequently fusing the resulting sodamide with carbon :



Barium cyanide is manufactured by heating a mixture of barium hydroxide, barium carbonate, and coke in the electric furnace, so that barium carbide results. The fused mass is then allowed to cool to a temperature at which it just solidifies, when it is exposed to an atmosphere of nitrogen, which converts the carbide into cyanide :



Finally, hydrogen cyanide is formed on passing a mixture of acetylene and nitrogen over the electric arc :



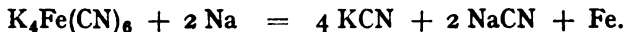
The older methods of preparing potassium cyanide consisted in heating potassium ferrocyanide (p. 218) either alone :



with potassium carbonate, whereby potassium cyanate (p. 223) is simultaneously produced :

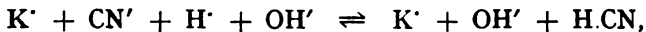


or with metallic sodium, whereby a mixture of potassium and sodium cyanides is formed :



Cyanides, in their reactions, show some analogy with chlorides ; in fact, the radicle —CN , in inorganic qualitative analysis, is classified with the halogens. Silver cyanide AgCN is a white precipitate, insoluble in dilute nitric acid, formed on adding silver nitrate to a solution of a cyanide.

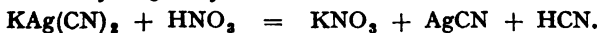
Aqueous solutions of sodium or potassium cyanide always show an alkaline reaction, and emit the odour of hydrocyanic acid. This is due to the fact that hydrogen cyanide is dissociated to only a very slight extent :



and being volatile, it slowly escapes from solution, leaving increasing quantities of alkali hydroxide in solution, until an equilibrium mixture is produced.

Tests for the detection of cyanides are the " Prussian Blue test " described on page 53, and the following :—if dilute nitric acid be added to a solution of a cyanide, hydrogen cyanide is liberated, so that a drop of silver nitrate solution on the under-side of a watch-glass covering the beaker containing the cyanide is rendered turbid by a precipitate of silver cyanide. A further test is to distil the cyanide solution with a small quantity of dilute sulphuric acid, and to add to the distillate, which contains hydrocyanic acid, a drop of yellow ammonium sulphide solution. Ammonium thiocyanate $\text{NH}_4\text{S.CN}$ (p. 227) is thereby formed ; this can be detected by acidifying with hydrochloric acid, boiling to expel hydrogen sulphide, and adding ferric chloride, which produces an intense red coloration.

Alkali cyanides are capable of forming double compounds with the cyanides of some heavy metals. Thus silver cyanide dissolves in a solution of potassium cyanide forming the soluble double salt KCN.AgCN or $\text{KAg}(\text{CN})_2$, known as potassium argenticyanide, which is decomposed by dilute nitric acid, yielding silver cyanide and hydrogen cyanide :



Similarly aurous cyanide AuCN forms sodium aurocyanide NaAu(CN)_2 with a solution of sodium cyanide. This fact is utilised in the "cyanide process" for the recovery of gold from the finely-divided gold "sludge" obtained by washing crushed auriferous rocks. The sludge is mixed with aqueous sodium (or potassium) cyanide and exposed to the air, when the gold enters into solution :

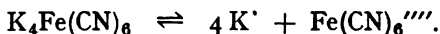
$4 \text{ Au} + 8 \text{ NaCN} + \text{O}_2 + 2 \text{ H}_2\text{O} = 4 \text{ NaAu(CN)}_2 + 4 \text{ NaOH}$,
from which it can be deposited electrolytically.

Mercuric cyanide Hg(CN)_2 is notable in that it is entirely undissociated in aqueous solution, and hence fails to give the tests characteristic of either mercuric salts or of cyanides.

Potassium ferrocyanide $\text{K}_4\text{Fe(CN)}_6$ was, until a few years ago, the source of all the cyanides employed industrially and in the laboratory. It is still manufactured by fusing a mixture of nitrogenous animal matter—such as blood, leather, horn, and so forth—and potassium carbonate, with scrap-iron. After fusion, the mass is treated with water, and the solution filtered and concentrated, when potassium ferrocyanide crystallises in large yellow tables $\text{K}_4\text{Fe(CN)}_6 \cdot 3 \text{ H}_2\text{O}$.

Ferrocyanides are not decomposed by acids in the way that argenticyanides are ; on adding hydrochloric acid to a solution of potassium ferrocyanide, no hydrogen cyanide is liberated ; the quadrivalent group $(\text{FeCN})_6$ functions as a whole, and hydrogen ferrocyanide $\text{H}_4\text{Fe(CN)}_6$ is stable in solution.

Potassium ferrocyanide ionises in solution in the sense of :

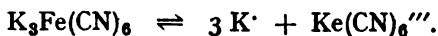


The ferric salt $\text{Fe}_4[\text{Fe(CN)}_6]_3$ is a blue precipitate, formed on adding ferric chloride to an acid solution of a ferrocyanide. It is generally known as Prussian Blue.

On passing chlorine into a solution of potassium ferrocyanide, **potassium ferricyanide** $\text{K}_3\text{Fe(CN)}_6$ is produced :



This is a crystalline substance of deep orange colour ; it is occasionally employed by the organic chemist as a mild oxidising agent. It is ionised in solution :

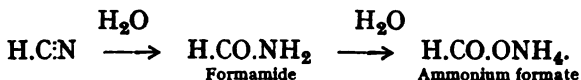


On heating potassium ferrocyanide with nitric acid, and then neutralising with soda, **sodium nitroprusside** is formed; this is a red crystalline salt of the composition $\text{Na}_2\text{Fe}(\text{CN})_6\text{NO} \cdot 2\text{H}_2\text{O}$. This complex salt is employed for detecting small quantities of sulphur, since it develops an intense violet coloration with dilute alkaline solutions of sulphides (p. 54).

HYDROGEN CYANIDE AND NITRILES

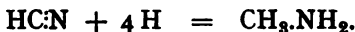
Hydrogen cyanide (*hydrocyanic acid* or *prussic acid*) $\text{H}-\text{C}\equiv\text{N}$, which is liberated from alkali cyanides by the action of even the weakest acids, is an intensely poisonous liquid which boils at 26° and is readily soluble in water. It hardly merits the epithet "acid," for an aqueous solution barely reddens blue litmus paper.

It forms the first member of the series of *nitriles* of fatty acids $\text{C}_n\text{H}_{2n+1}\text{C}\cdot\text{N}$, and is in fact itself the nitrile of formic acid, being produced by the dehydration of formamide (p. 174). Its aqueous solution slowly decomposes, yielding ammonium formate. Hydrolysis can also be carried out so that formamide is produced as an intermediate stage :



It yields formic acid on treatment with strong hydrochloric acid. When, on the other hand, cyanides are warmed with concentrated sulphuric acid, carbon monoxide is evolved, due to the dehydration (p. 163) of the formic acid initially formed. On boiling with alkali hydroxides, a formate and ammonia are produced (p. 162).

It may be reduced to methylamine by treatment with zinc and hydrochloric acid :

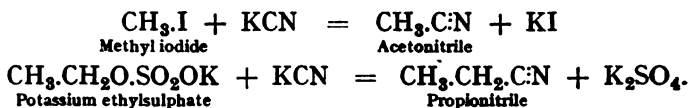


Its faculty of combining with aldehydes and ketones has already been discussed (p. 143).

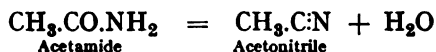
Nitriles are in every way true homologues of hydrogen cyanide. The chief modes of formation have already been

mentioned in different connections; they may here be summarised :

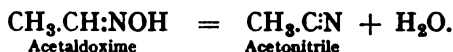
(1) Action of alkyl halides or alkyl esters of inorganic acids upon alkali cyanides, by boiling in alcoholic or aqueous solution :



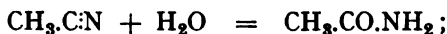
(2) Dehydration of acid amides by distillation with phosphorus pentoxide :



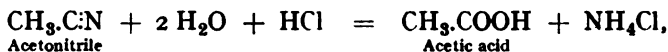
(3) Dehydration of aldoximes (p. 144) by heating with acetic anhydride :



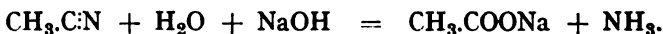
Nitriles may, like hydrogen cyanide, be hydrolysed and reduced. Hydrolysis is effected by acid and alkaline reagents and by pure water. On heating with water to 180° in a closed vessel, acid amides are formed :



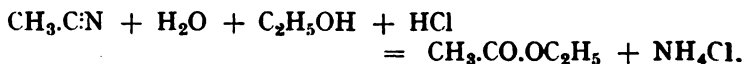
at higher temperatures the amides themselves slowly take up water, so that ammonium salts are produced (p. 173). Complete hydrolysis is effected more rapidly by heating with aqueous mineral acids :



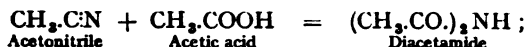
or alkalis :



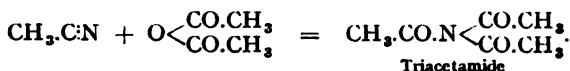
If nitriles be boiled with mineral acids in moist alcoholic solution, esters are formed :



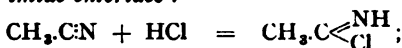
On heating with organic acids, a *di-acyl* derivative of ammonia is produced :



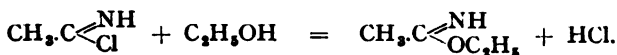
whilst with acid anhydrides, *tri-acyl* derivatives are formed :



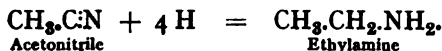
Hydrogen chloride combines with nitriles, forming addition-products termed *imide-chlorides* :



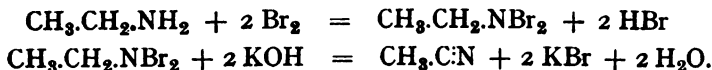
these react with alcohols, yielding *iminoethers* :



Nitriles may be reduced to primary amines either by treatment with zinc and hydrochloric acid (Mendius's reaction), or better, by adding sodium to a solution of the nitrile in boiling absolute alcohol :



The reverse change can be brought about by treating a primary amine containing the grouping $\text{—CH}_2\text{.NH}_2$ with bromine and subsequently distilling the resulting dibromoamine with aqueous potassium hydroxide :

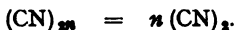


Nitriles are colourless liquids or solids, the lower members of the series being somewhat soluble in water. They are by no means so poisonous as hydrogen cyanide. **Acetonitrile** (*methyl cyanide*) $\text{CH}_3\text{.CN}$ boils at 81° ; **propionitrile** (*ethyl cyanide*) $\text{CH}_3\text{.CH}_2\text{.CN}$ boils at 98° .

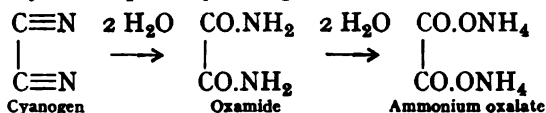
Cyanogen N:C.C:N is prepared by heating mercuric cyanide :



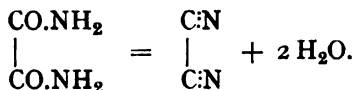
An amorphous substance—*paracyanogen*—is simultaneously produced. This is a polymer of cyanogen $(\text{CN})_{2n}$, which breaks down into cyanogen on strongly heating :



Cyanogen is a poisonous gas, which dissolves readily in water and burns in air with a violet flame. In aqueous solution it gradually decomposes, yielding ammonium oxalate :



From this behaviour, cyanogen is obviously the double nitrile of oxalic acid ; this is borne out by its formation from oxamide, on heating alone, or better, with phosphorus pentoxide :



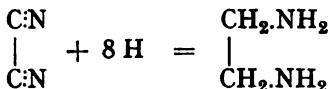
On treatment with alkalis it yields a mixture of cyanide and cyanate :



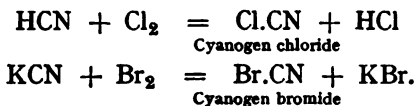
a reaction recalling the behaviour of the halogens under the same conditions :



On reduction it yields ethylenediamine (p. 205) :



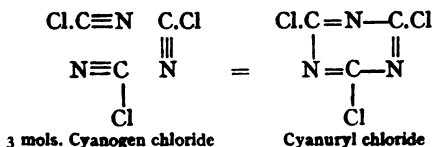
Cyanogen forms compounds with the halogens ; these are, however, not prepared by bringing together halogen and cyanogen, but by the action of halogens upon hydrogen cyanide or potassium cyanide in aqueous solution :



Cyanogen chloride Cl.CN boils at 15° . **Cyanogen bromide** Br.CN melts at 52° and boils at 61° . On treatment with alkalis they yield cyanates :

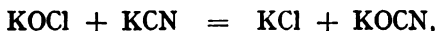


They spontaneously polymerise to trimolecular products, which may be regarded as the halides of cyanuric acid (p. 224) :



CYANATES

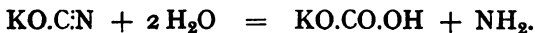
Potassium cyanate $\text{KO.C}\equiv\text{N}$ is formed by the oxidation of potassium cyanide. This may be effected either in solution, by means of potassium permanganate or hypochlorite :



or in the dry way, by treating potassium cyanide in the fused state with oxides of heavy metals such as lead or tin :

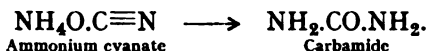


The most convenient method of preparation consists in heating an intimate mixture of potassium ferrocyanide and potassium bichromate, whereby the cyanide formed by the decomposition of the ferrocyanide (p. 218) is oxidised by the bichromate as fast as it is produced. Potassium cyanate is a white crystalline solid, soluble in water and alcohol, which is gradually decomposed by moisture, being converted into potassium hydrogen carbonate and ammonia :

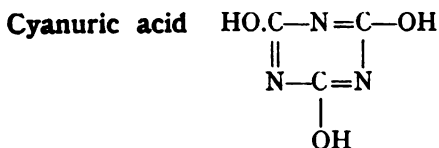
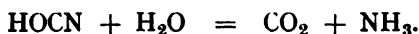


Ammonium cyanate NH_4OCN is of interest by reason of the isomeric change which it undergoes on boiling with water, whereby it is converted into carbamide $\text{NH}_2\text{.CO.NH}_2$ (p. 180). The reaction may be expressed as simultaneous dehydration of the $-\text{ONH}_4$ grouping, as in the formation of acid amides

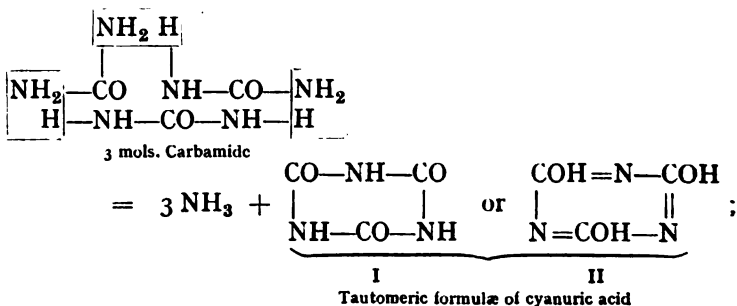
from ammonium salts ($-\text{CO.O.NH}_4 \rightarrow -\text{CO.NH}_2 + \text{H}_2\text{O}$), and hydration of the $-\text{C}\equiv\text{N}$ radicle ($-\text{C}\equiv\text{N} + \text{H}_2\text{O} = -\text{CO.NH}_2$), so that the change may be expressed :



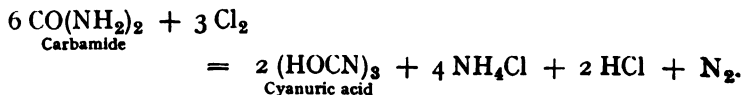
Cyanic acid $\text{HO.C}\equiv\text{N}$ is a pungent liquid which is stable only below 0° . Above this temperature it polymerises with almost explosive violence to **cyamelide**, a white mass resembling porcelain. Cyanic acid in aqueous solution decomposes rapidly into carbonic acid and ammonia :



can be produced in a variety of ways. It is slowly precipitated when dilute acetic acid is added to a solution of potassium cyanate ; it is also formed on heating carbamide either alone :



or in presence of chlorine :

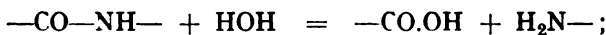


It is also obtained by heating ammonia with an excess of carbonyl chloride :

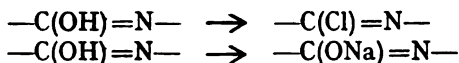


These reactions clearly show its relationship to carbamide : it may be regarded either as tricarbimide (I), a cyclic tri-imide of carbonic acid, or as the corresponding trihydroxylic compound (II), as formulated above. It is often doubtful whether substances of this nature should be formulated with the grouping —CO—NH— , or the alternative —C(OH)=N— , in which the hydrogen atom has changed its position.

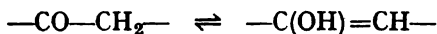
Compounds containing this grouping sometimes behave in their reactions as if both forms were present. They can be hydrolysed in the manner usual with amides and imides :



they also behave as if they contained hydroxyl groups ; for instance, they yield chlorides or metallic salts :

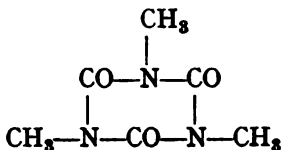


Compounds which can thus react as if they possessed two different chemical constitutions, are termed *tautomeric*. In tautomeric substances the changes in constitution are due to the possibility of shifting the position of a hydrogen atom. A grouping in which this frequently occurs is :

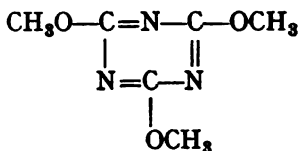


In cyanuric acid itself the chief reactions are those corresponding with the hydroxylic formula. It is instructive to note, however, that two sets of alkyl derivatives of cyanuric acid are known. Only hydrogen atoms are capable of oscillating between two positions, so that if the hydrogen atoms in cyanuric acid be replaced by methyl groups, two different compounds are produced, according to the conditions of

formation, in which the methyl groups are attached respectively to oxygen and to nitrogen atoms :

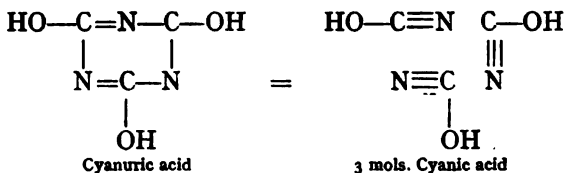


I



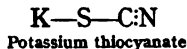
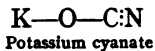
II

Cyanuric acid is soluble in water and crystallises with two molecules of water : $\text{C}_3\text{H}_3\text{O}_3\text{N}_3 \cdot 2 \text{H}_2\text{O}$. On heating, it first loses the water of crystallisation, and then breaks down into cyanic acid :



On treatment with phosphorus pentachloride it is converted into cyanuryl chloride, the trimolecular polymer of cyanogen chloride (p. 223).

THIOCYANATES are the sulphur analogues of cyanates :



They are sometimes called "sulphocyanides," from their formation by fusing alkali cyanides with sulphur :



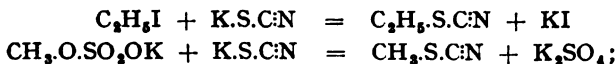
Characteristic of the thiocyanates is the intense red colour developed with solutions of ferric salts, due to the formation of double salts such as $9 \text{KSCN} \cdot 2 \text{Fe}(\text{SCN})_3$. The thiocyanates are more stable than the cyanates, and remain without decomposition in aqueous solution for an indefinite period.

Ammonium thiocyanate $\text{NH}_4.\text{S.C}\equiv\text{N}$ is formed on treating a solution of hydrogen cyanide with yellow ammonium sulphide; a more convenient method of preparation is to heat carbon bisulphide with alcoholic ammonia:

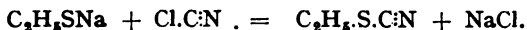


It is a crystalline substance, soluble in water and in alcohol, which melts at about 150° . On heating to 170° – 180° it undergoes an intramolecular rearrangement similar to that of ammonium cyanate, yielding thiocarbamide (p. 183).

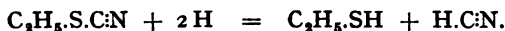
Alkyl thiocyanates $\text{R.S.C}\equiv\text{N}$ in which an alkyl radicle replaces the metal, may be prepared by two different methods, which clearly show their constitution: firstly by the action of alkyl halides, or alkyl esters of inorganic salts, such as metallic alkylsulphates $\text{RO.SO}_3\text{OK}$, upon alkali thiocyanates:



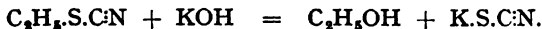
secondly by the interaction of cyanogen halides upon metallic mercaptides (p. 210):



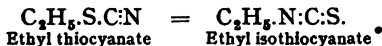
They are oily liquids of unpleasant odour. Their constitution is established by treatment with nascent hydrogen—for instance, with zinc and dilute sulphuric acid—whereby they are decomposed into mercaptans and hydrogen cyanide:



From this it is clear that the alkyl group is directly united to the sulphur atom. On boiling with alcoholic potash they yield the alcohol and potassium thiocyanate:

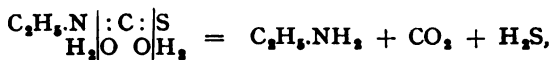


On heating to 180 – 190° , alkyl thiocyanates undergo an isomeric change, by which **alkyl isothiocyanates** R.N:C:S are produced:

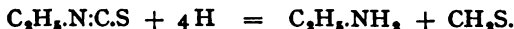


Alkyl isothiocyanates are also termed "mustard oils," because **allyl isothiocyanate** $\text{CH}_2:\text{CH.CH}_2.\text{N:C:S}$ forms the chief constituent of the oil of mustard. Their constitution is proved by their behaviour on heating with dilute acids or with water, when

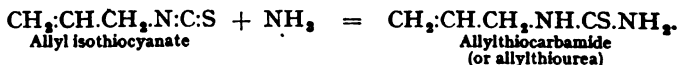
they break up into primary amines, carbon dioxide, and hydrogen sulphide :



this showing that the alkyl group is directly attached to the nitrogen atom. The same fact is also indicated by their behaviour on reduction, when they yield primary amines and *thioformaldehyde* CH_3S , the sulphur analogue of formaldehyde :



They combine with ammonia, yielding *alkyl-thiocarbamides* :



ALKYL ISOCYANATES

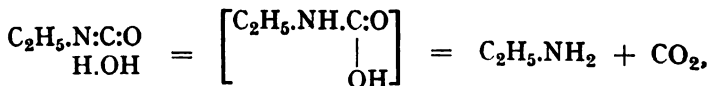
If we treat potassium cyanate with an alkyl halide we might expect to obtain an *alkyl cyanate* $\text{R}\cdot\text{O}\cdot\text{C:N}$. Such is, however, not the case, for an *alkyl isocyanate* is produced. It is probable that as fast as the normal cyanate is formed, it undergoes a rearrangement similar to that undergone by the thiocyanate on heating :



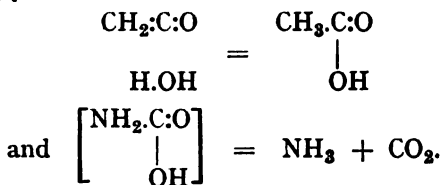
Alkyl isocyanates are more reactive than alkyl isothiocyanate, just as metallic cyanates are more unstable than metallic thiocyanates. Their behaviour is, in fact, closely analogous to that of keten (p. 172), with which they have a certain structural analogy :



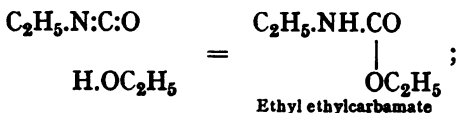
With water they yield substituted carbamic acids, which, like carbamic acid itself (p. 181), breaks up at once into primary amine and carbon dioxide :



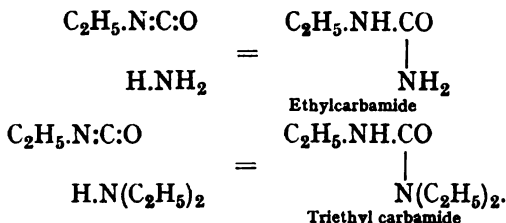
analogous to :



With alcohols they yield esters of substituted carbamic acids, or substituted urethanes (cf. urethanes, p. 181) :



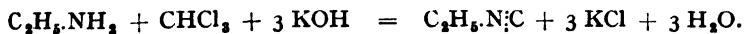
and with ammonia, or with primary and secondary amines they yield substituted carbamides :



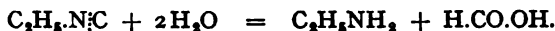
Thus alkyl isocyanates react, like keten, with all substances containing a hydroxyl group, and with bases containing a hydrogen atom attached to nitrogen.

ALKYL ISOCYANIDES, also called **carbylamines** or **isonitriles**, R.N:C may be regarded as carbon monoxide in which the oxygen atom is replaced by the radicle R.N . As we have neither data nor necessity for deciding between the two formulæ $\text{C}\equiv\text{O}$ and C=O for carbon monoxide, it is immaterial which of the two formulæ we employ for the isocyanides. It is customary, in conformity with the postulate of constant quadrivalency of the carbon atom, to employ for isocyanides the formulation $-\text{N}\equiv\text{C}$, in which the carbon atom is represented as quadrivalent.

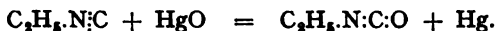
Isocyanides are formed by warming a primary amine with alcoholic potash and chloroform :



Isocyanides are colourless oils, possessing most unpleasant and penetrating odours. On heating with water or aqueous acids they yield primary amines and formic acid :



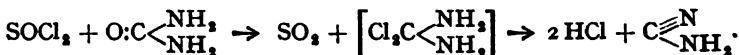
They may be oxidised by mercuric oxide to isocyanates :



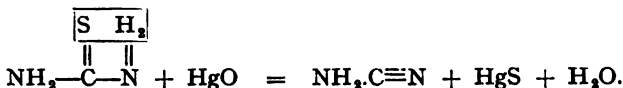
Cyanamide $\text{H}_2\text{N.C}\equiv\text{N}$ may be regarded as the nitrile of carbamic acid. It is formed by the interaction of cyanogen chloride with ammonia :



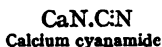
by the dehydration of carbamide by means of thionyl chloride :



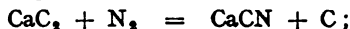
or by removal of the elements of hydrogen sulphide from thio-carbamide by means of mercuric oxide :



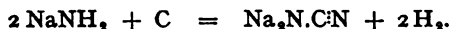
It is a white crystalline solid, very soluble in water, alcohol, or ether. It is capable of forming metallic derivatives, in which both hydrogen atoms are replaced by metal :



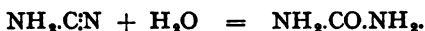
Calcium cyanamide is formed by heating calcium carbide in an atmosphere of nitrogen :



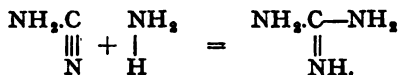
sodium cyanamide is produced as a by-product in the manufacture of sodium cyanide from sodamide (p. 216) :



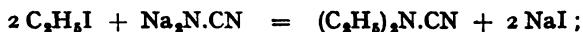
Cyanamide is hydrolysed on warming with aqueous mineral acids, yielding carbamide :



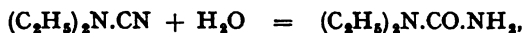
With ammonia it yields guanidine (p. 182) :



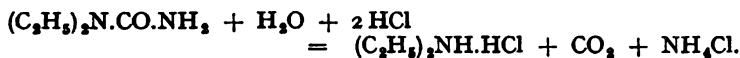
If sodium or calcium cyanamide be treated with alkyl halides or alkyl esters of inorganic acids, **dialkyl cyanamides** are formed :



these, on hydrolysis, yield asymmetrical dialkyl carbamides :



which, on further hydrolysis, yield secondary amines :



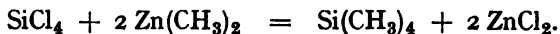
CHAPTER XVII

ALKYL DERIVATIVES OF METALS AND NON-METALS

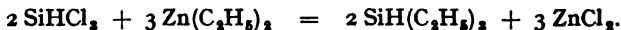
ORGANIC DERIVATIVES OF SILICON AND TIN

Silicon, which occurs in the Periodic Table in the same group as carbon, shows many analogies with this element. It forms a tetrahydride, *silicane* SiH_4 corresponding with methane, a tetrachloride SiCl_4 corresponding with carbon tetrachloride; and even a compound $\text{H}_3\text{Si}-\text{SiH}_3$ corresponding with ethane. But silicon fails to show any readiness to unite with itself so as to form long silicon chains, in the way that carbon forms carbon chains. For this reason there is no "organic" chemistry of silicon analogous to that of carbon compounds.

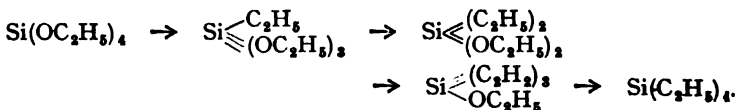
Nevertheless, alkyl derivatives of silicon can be prepared. Thus **tetramethylsilicane**, or **silicon tetramethyl** $\text{Si}(\text{CH}_3)_4$, also called *silico-pentane*, is produced by the interaction of silicon tetrachloride and zinc methyl (p. 234) :



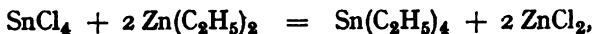
Similarly, silicochloroform SiHCl_3 , on treatment with zinc ethyl, yields **triethylsilicane**, or *silicoheptane* :



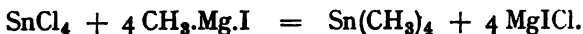
It may here be mentioned that esters of silicic acid exist: such is **ethyl orthosilicate** $\text{Si}(\text{OC}_2\text{H}_5)_4$. These react with zinc alkyls, which successively replace the alkoxyl (*e.g.* ethoxyl $-\text{OC}_2\text{H}_5$) groups by alkyl groups :



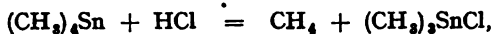
Tin, in its quadrivalent condition, is also capable of forming alkyl derivatives. These are prepared in the same way as the preceding—from stannic chloride, either with zinc alkyls :



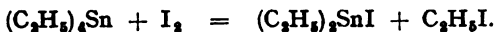
or with alkyl magnesium halides (p. 235) :



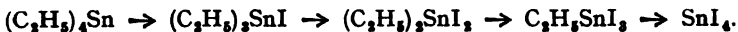
Tin alkyls are slowly decomposed by hydrochloric acid, yielding saturated hydrocarbons :



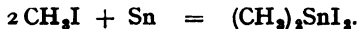
and more rapidly by iodine, yielding alkyl iodides :



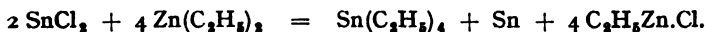
By employing the requisite amount of iodine, the alkyl groups may thus be successively removed :



The alkyl-stannic iodides are also formed by heating tin with alkyl iodides :



If dry stannous chloride be treated with zinc alkyls, alkyl derivatives of quadrivalent tin are formed, with separation of metallic tin :

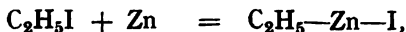


Tin tetramethyl $\text{Sn}(\text{CH}_3)_4$ is a colourless oil, which boils at 78° .
Tin tetraethyl $\text{Sn}(\text{C}_2\text{H}_5)_4$ boils at 181° .

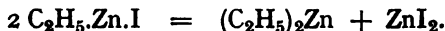
ALKYL DERIVATIVES OF ZINC AND MAGNESIUM

More important than the organic derivatives of silicon and tin are the **zinc alkyls**, which have been employed for the preparation of some of the substances above mentioned.

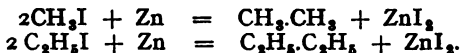
Zinc alkyls are produced by the action of alkyl iodides upon zinc filings. The reaction proceeds more readily if the zinc, which must be in excess, be mixed with finely-divided copper, which causes an electric "couple" to be formed. The first stage of the process is the formation of **alkyl zinc iodide** :



which on heating breaks down into zinc iodide and zinc alkyl :



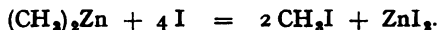
All operations must be carried out in a stream of inert gas, such as dry hydrogen or nitrogen, for zinc alkyls are so rapidly oxidised on exposure to the air that they take fire. It is essential that an excess of zinc be present, otherwise higher hydrocarbons will be exclusively formed, by simple elimination of halogen :



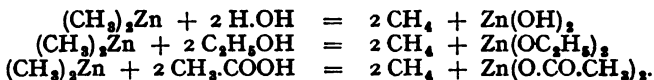
The zinc alkyls are colourless liquids, which may be distilled unchanged. **Zinc methyl** $(\text{CH}_3)_2\text{Zn}$ boils at 46° ; **Zinc ethyl** $(\text{C}_2\text{H}_5)_2\text{Zn}$ boils at 118° . They burn in air with a white flame, yielding carbon dioxide, water and zinc oxide :



They also take fire in an atmosphere of chlorine, yielding zinc chloride. If they be treated with iodine in solution in some inert solvent, such as petroleum, the reaction proceeds more smoothly, zinc iodide and alkyl iodide being formed :

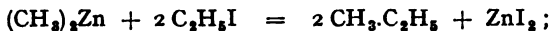


They react at once with water and with alcohols—in fact with all substances containing hydroxyl groups—yielding the corresponding saturated hydrocarbon :



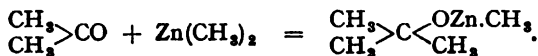
A similar reaction takes place with hydrochloric acid.

With alkyl halides, hydrocarbons are formed :



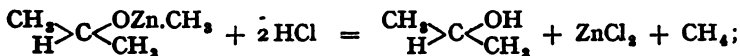
and by selecting suitable halogen derivatives, more complex hydrocarbons can be synthesised.

An important property of the zinc alkyls is that of addition to carbonyl compounds (aldehydes and ketones), by which one of the alkyl groups attaches itself to the carbonyl carbon atom :



These addition products may be decomposed by water or by dilute

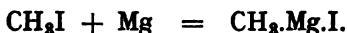
acids, whereby alcohols are formed. Aldehydes yield secondary alcohols :



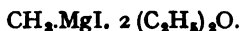
ketones yield tertiary alcohols.

It can thus be seen how zinc alkyls have been of the greatest assistance to synthetical organic chemistry. Their main disadvantage is the experimental difficulty attending their use, due to their inflammability.

Of recent years the zinc alkyls have been supplanted in their synthetical applications by the *ALKYL MAGNESIUM HALIDES*, commonly called *GRIGNARD'S REAGENTS*. These are formed when an alkyl halide is added to a suspension of magnesium turnings in dry ether :



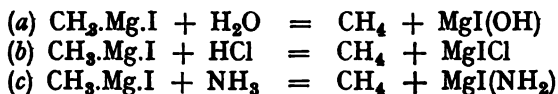
The reaction often takes place with considerable evolution of heat. The product is, as a rule, soluble in ether. On evaporating off the excess of ether, a solid product remains, which contains two molecules of ethyl ether to one molecule of alkyl magnesium halide, *e.g.* :



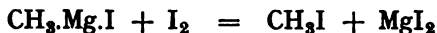
The ether is very firmly retained in this complex, being only partially removed by heating in a vacuum to 125°.

The alkyl magnesium halides, which are always employed in solution in the ether in which they were prepared, afford reactions similar to those of the zinc alkyls. The various types of reaction may here be summarised :

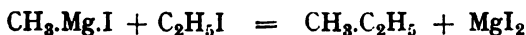
I. With various inorganic hydrogen compounds :



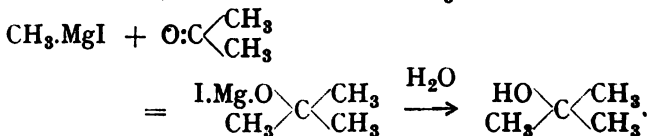
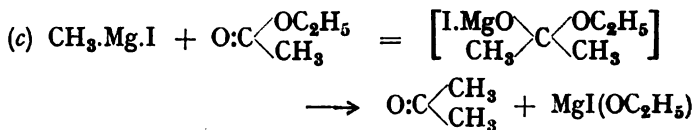
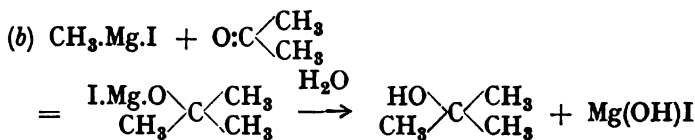
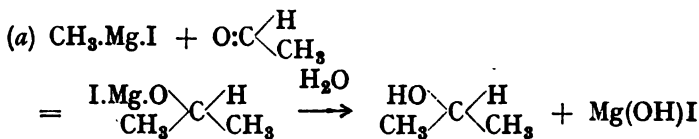
II. With iodine :



III. With alkyl halides :

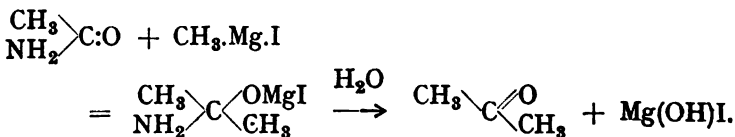


IV. With aldehydes, ketones, and esters :



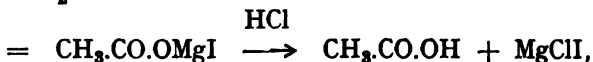
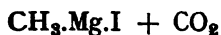
From the above equations it can be seen that hydroxylic compounds, ammonia, and hydrogen halides give rise to saturated hydrocarbons corresponding with the original alkyl group ; iodine regenerates the alkyl iodide ; other alkyl iodides lead to the formation of higher hydrocarbons, aldehydes and formic esters give secondary alcohols ; ketones and fatty esters give tertiary alcohols.

Ketones and acids may also be prepared from alkyl magnesium halides. If an amide be treated with an alkyl magnesium halide, an addition-product is obtained which yields a ketone on treatment with water :



If dry carbon dioxide be passed into an ethereal solution

of an alkyl magnesium halide, a precipitate is formed. This consists of a salt of a carboxylic acid, which can be decomposed by dilute hydrochloric acid :



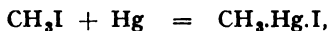
so that this constitutes a direct method for passing from an alkyl halide to a carboxylic acid containing one more carbon atom in the molecule.

The value of the Grignard reactions in organic synthesis has been incalculable, owing to their wide applicability and the ease with which the alkyl magnesium compounds can be prepared and manipulated.

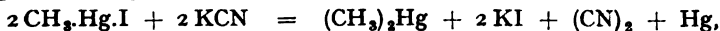
Magnesium alkyls $\text{R}.\text{Mg}.\text{R}$ are unknown.

ORGANIC DERIVATIVES OF MERCURY.

Alkyl iodides react slowly with metallic mercury, forming **alkyl mercuric iodides** :



which are converted into **mercury alkyls** either by distillation with potassium cyanide :



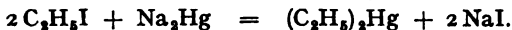
or by the action of zinc alkyls :



They are also produced by the interaction of mercuric chloride with zinc alkyls :



and by treating sodium amalgam with alkyl iodides :



Mercury alkyls are colourless liquids, insoluble in water, which possess no pronounced odour but are terribly poisonous. They differ from zinc alkyls in being stable towards air and water.

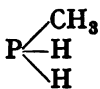
ORGANIC DERIVATIVES OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

These elements, which find their places in the Periodic Table in the same groups as nitrogen, are, with the exception

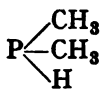
of bismuth, capable of forming hydrides PH_3 , AsH_3 , SbH_3 , which diminish in stability and basic character, and increase in oxidisability, with ascending atomic weight of the element. The hydrocarbons in these hydrides can, like those in ammonia, be replaced by alkyl radicles :



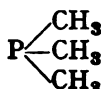
Phosphine



Methyl phosphine

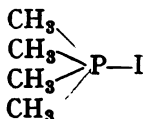


Dimethyl phosphine



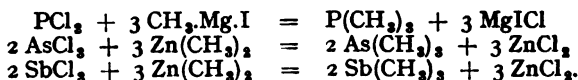
Trimethyl phosphine

Further, alkyl derivatives of salts of some of these elements in their quinquivalent form, such as phosphonium iodide PH_4I , can be prepared :



Tetramethylphosphonium iodide

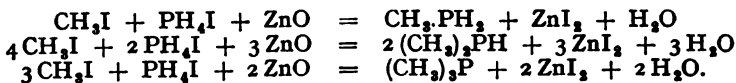
A general method for their preparation consists in causing alkyl magnesium halides or zinc alkyls to react with the halides of the elements :



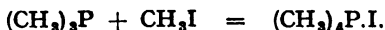
Even bismuth, the hydride of which is too unstable to exist, can be induced to form alkyl derivatives :



The alkylphosphines are, like phosphine itself, less strongly basic than the alkylamines and ammonia, and they cannot well be prepared by the interaction of phosphine and alkyl halides alone. Primary and secondary phosphines are, however, formed on heating phosphonium iodide with alkyl halides in presence of zinc oxide, which removes hydrogen iodide as fast as it is produced :

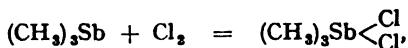


The trialkylphosphines, prepared by the method above indicated, unite directly with alkyl iodides, yielding **quaternary phosphonium** iodides :

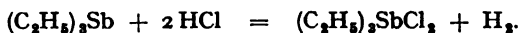


This is a liquid which oxidises so readily that it takes fire spontaneously in the air.

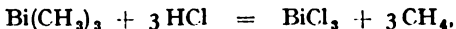
The **trialkylstibines** R_3Sb are likewise liquids which take fire on exposure to air. Their chemical behaviour somewhat resembles that of a bivalent metal, such as magnesium or zinc, since they readily unite with chlorine, forming dichlorides :



and displace hydrogen from hydrochloric acid :



The **trialkyl bismuthines** R_3Bi are also liquids which inflame spontaneously in the air. So unstable are they that they explode when heated under atmospheric pressure, although they can be distilled under reduced pressure. On treatment with hydrochloric acid they are broken up into bismuth chloride and paraffin hydrocarbons :



resembling the tin and zinc alkyls in this behaviour.

CHAPTER XVIII

HYDROXYACIDS

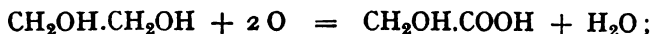
HYDROXYACIDS are compounds which contain both carboxyl (—COOH) and hydroxyl (—OH) groups. They thus partake of the nature of both acids and alcohols.

MONOCARBOXYLIC HYDROXYACIDS are fatty acids in which one of the hydrogen atoms, other than that contained in the carboxyl group, is replaced by a hydroxyl group. Exception must be made in the case of formic acid, replacement of the single hydrogen atom giving rise to carbonic acid (p. 163).

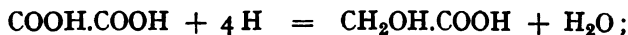
The simplest hydroxyacid is the monohydroxy derivative of acetic acid—glycollic acid :



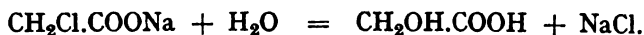
Glycollic acid $\text{CH}_2\text{OH.COOH}$ may be prepared in several ways which make clear its constitution. It is formed by the careful oxidation of ethylene glycol (p. 129) :



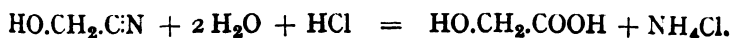
by electrolytic reduction of oxalic acid :



and by boiling sodium or potassium monochloroacetate in aqueous solution :

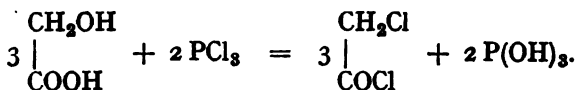


A further method of preparation consists in hydrolysis of the cyanohydrin of formaldehyde :

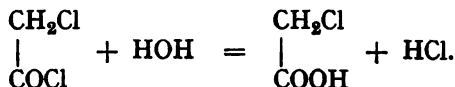


R

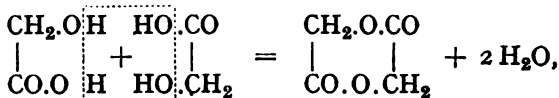
Glycollic acid is a crystalline solid, which melts at 74° and is very soluble in water and in alcohol. Its double function of alcohol and acid is clearly shown by the action of phosphorus trichloride: both hydroxyl groups are replaced by chlorine, chloroacetyl chloride being formed:



The chloroacetyl chloride, on treatment with water, loses one of the chlorine atoms as hydrogen chloride, after the manner of acid chlorides; the other behaves as the chlorine atom of an alkyl chloride, and remains firmly bound to its carbon atom:



On heating by itself, glycollic acid does not volatilise as such, but loses water in the sense that two molecules esterify each other. The product which passes over is known as **glycolide**:



which may be reconverted into glycollic acid on hydrolysis by prolonged heating with water:

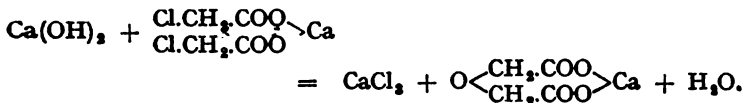
On oxidation, glycollic acid yields firstly glyoxylic acid (p. 258), and then oxalic acid:



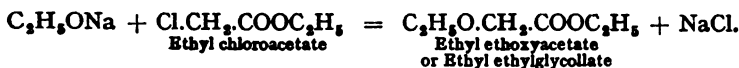
Like all carboxylic acids, glycollic acid forms esters with alcohols in the ordinary way. **Ethyl glycolate** $\text{CH}_2\text{OH} \cdot \text{COOC}_2\text{H}_5$ is a liquid boiling at 160° . Like all alcohols, glycollic acid can form ethers: **diglycollic acid**



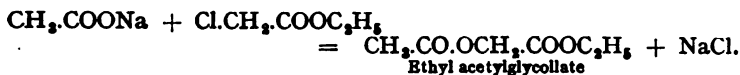
is formed, together with glycollic acid, on boiling chloroacetic acid with a suspension of lime in water :



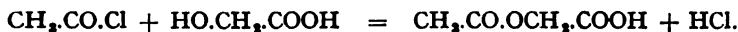
The ethyl ether of the ethyl ester of glycollic acid is formed on treating ethyl chloroacetate with alcoholic sodium ethylate :



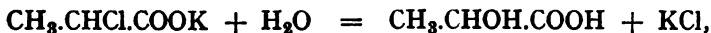
Similarly, the acetate of the ethyl ester of glycollic acid is formed by treating ethyl chloroacetate with sodium acetate :



The free acid, *acetylgllycollic acid*, is produced by the action of acetyl chloride on glycollic acid :



The next homologue is **lactic acid**, which is *α-hydroxypropionic acid* $\text{CH}_3\text{CHOH.COOH}$. As its name implies, it is present in sour milk. Synthetically, lactic acid may be prepared by the general methods stated for the preparation of glycollic acid, as for instance, by boiling an aqueous solution of potassium *α*-chloropropionate :



or by hydrolysis of acetaldehyde cyanohydrin (lactonitrile, p. 143) by means of aqueous acid :



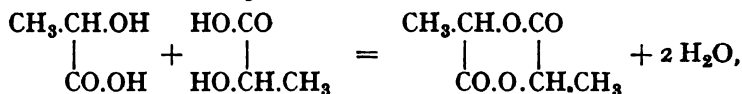
On the manufacturing scale it is produced by the acid fermentation of sugar. The conditions are the same as in the manufacture of butyric acid (p. 165)—putrid cheese and sour milk, which contain the necessary ferment, and calcium carbonate or zinc carbonate, which neutralise the acid as fast as it is produced, are added to a sugar solution maintained at 35–45°.

As soon as the sparingly soluble lactate of calcium or zinc separates from the mixture, it is removed; were it allowed to remain, a secondary action would take place, whereby butyric acid would be produced.

Lactic acid is also formed, in considerable quantity, from sugars without the agency of ferments—merely by the action of alkali. The process is the effect of a complicated series of reactions involving successive alternation of dehydration and hydration.

Lactic acid, when pure, melts at 18° , but exists generally as a syrup, since it is extremely hygroscopic. It is isolated from the calcium or zinc salts, obtained as indicated above, by adding exactly the requisite quantity of dilute sulphuric acid, evaporating the solution until it contains fifty per cent. of the free lactic acid, and then extracting this with ether or amyl alcohol.

It is a matter of difficulty to obtain chemically pure lactic acid, since on heating it is converted into lactide:

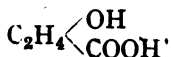


and can be distilled unchanged only under a pressure of less than 1 mm. of mercury.

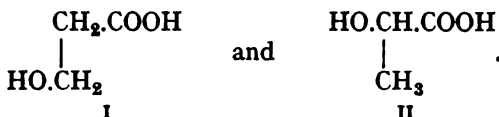
The chief reactions of lactic acid are similar to those of glycollic acid. On distillation with phosphorus trichloride or pentachloride it yields α -chloropropionyl chloride $\text{CH}_3.\text{CHCl}.\text{COCl}$. On heating to 130° with dilute sulphuric acid it breaks down with acetaldehyde and formic acid:



Sarcosarcolactic acid, an acid present in muscular tissue, is a substance closely resembling lactic acid, with the difference that it melts at 26° . It likewise possesses the simple molecular formula $\text{C}_3\text{H}_6\text{O}_3$, and is therefore isomeric with lactic acid. Moreover, the reactions which it undergoes leave no doubt that it contains a carboxyl group and a hydroxyl group, so that its composition may be expressed by

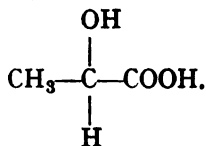


Now there are only two ways in which a structural formula can be written which will satisfy these conditions, namely :



Sarcolactic acid, on heating with dilute sulphuric acid, breaks up into acetaldehyde and formic acid in exactly the way as does lactic acid, so that the probability rests with the second formula. Furthermore, an acid which must from its synthesis obviously possess the constitution of the first formula, has been prepared (p. 246), and this differs entirely from sarcolactic acid in its chemical and physical properties, so that the first formula is excluded.

We are thus confronted with two distinct substances, lactic acid and sarcolactic acid, to both of which we must ascribe the same structural formula :

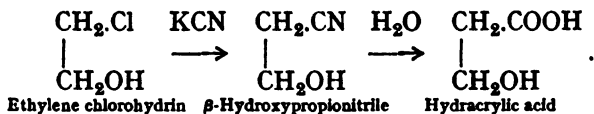


The clue to the solution of this problem is to be found in the fact that sarcolactic acid is optically active—it rotates the plane of polarised light to the right—whilst ordinary lactic acid, prepared from milk or by fermentation of sugar, is optically inactive. It will be recalled that in optically active amyl alcohol (p. 123) four different atoms or groups are attached to one and the same carbon atom, so that two spatial arrangements of these groups—such that they are non-superposable mirror-images—can be conceived. The same is the case with lactic acid. Sarcolactic acid is the *dextro* isomer, since it rotates polarised light to the right.

A third isomeric lactic acid has also been prepared by the action of certain ferments upon sugar. This would be identical with sarcolactic acid in chemical and physical properties, were it not that it rotates the plane of polarisation to the left—to the same extent, in fact, as sarcolactic acid rotates to the right.

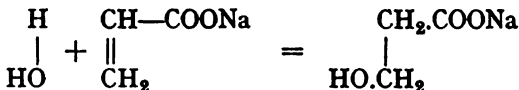
This is *laevo* lactic acid. On mixing equal quantities of sarco-lactic (*d*.lactic) acid and *l*.lactic acid, the product is identical with ordinary inactive lactic acid, which is therefore an equimolecular mixture of the two optically active isomeric lactic acids. This proof has been supplemented by the resolution—by methods to be described when discussing tartaric acid (p. 252)—of inactive lactic acid into the two optically active forms.

Still another hydroxyacid $C_3H_6O_3$ is known. This is **hydracrylic acid** or *β -hydroxypropionic acid* $CH_2OH.CH_2.COOH$, which has been prepared from ethylene chlorohydrin by the following series of reactions :



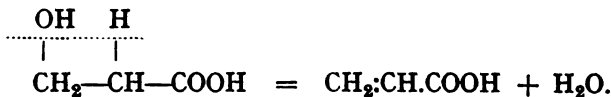
It is also formed by heating *β -iodopropionic acid* with water in the presence of silver oxide :

$2 I.CH_2.CH_2.COOH + H_2O + Ag_2O = 2 HO.CH_2.CH_2.COOH$,
and by heating acrylic acid (p. 168) with aqueous sodium hydroxide, whereby addition of water takes place :

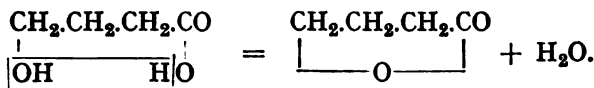


There is no asymmetric carbon atom in hydracrylic acid ; this is in accord with the fact that no optically active acid of the formula $CH_2OH.CH_2.COOH$ has ever been obtained.

Hydracrylic acid is a syrup which is very soluble in water. On heating alone it does not form a mutual ester as does lactic acid (lactide, p. 244), but loses water with formation of acrylic acid :



γ -Hydroxybutyric acid $CH_2OH.CH_2.CH_2.COOH$ is of interest in that on heating it loses one molecule of water and is converted into *γ -butyrolactone* :



This is a lactone or internal ester. On hydrolysis, the original hydroxy acid is regenerated.

δ-Hydroxyvaleric acid $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{COOH}$ also yields a lactone on heating.

It is a fact frequently observed that carbon chains tend to close themselves, whenever opportunity arises, into rings containing five or six members. Examples of this are : succinic anhydride (p. 190), glycolide, lactide. This is explained by the fact that five regular tetrahedra (cf. p. 122), when strung together to represent carbon chains, can assume a cyclic contour.

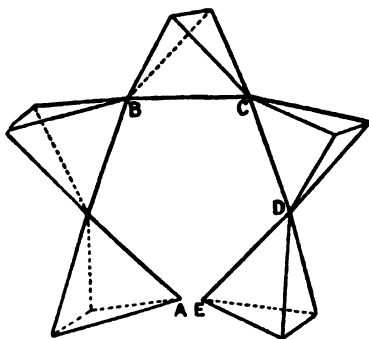
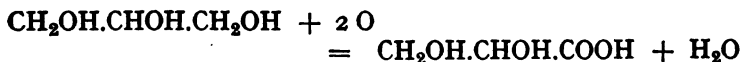


FIG. 8.

Glyceric acid $\text{CH}_2\text{OH}.\text{CHOH}.\text{COOH}$, the simplest dihydroxyacid, is produced by gentle oxidation of glycerol or acrylic acid :



It is a syrup, very soluble in water. Synthetically prepared, it is optically inactive ; active isomers can be prepared from it by the methods described below. On heating alone, it loses water, yielding pyruvic acid (p. 258).

DICARBOXYLIC HYDROXYACIDS

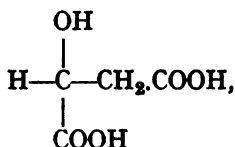
Malic acid, monohydroxysuccinic acid,



occurs in many unripe fruits, and was isolated for the first time from the juice of unripe apples, whence its name is derived.

On adding lime to the juice, the insoluble calcium salt is precipitated and can be purified by recrystallisation from dilute nitric acid. The free acid is prepared by adding to this salt exactly the requisite quantity of dilute sulphuric acid, removing the calcium sulphate, and concentrating the clear solution. The acid thus obtained is a hygroscopic crystalline solid which melts at 100° .

Malic acid contains an asymmetric carbon atom :

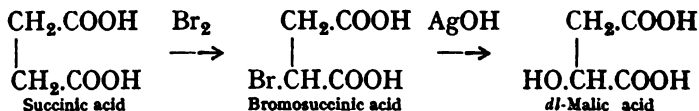


so that we can expect to find it to occur in optically active forms. The natural acid, prepared from apple juice, is *laevo-rotatory*. A *dextrorotatory* malic acid has also been prepared. The chemical properties of these two acids are identical ; in physical properties they differ only in the direction in which the plane of polarised light is rotated by their solutions.

A malic acid which is optically inactive may be synthesised in a variety of ways. Succinic acid (p. 189), on treatment with phosphorus trichloride, yields succinyl chloride ; this, on warming with the calculated quantity of bromine (cf. p. 160), is converted into monobromosuccinyl chloride :

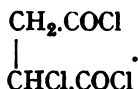


Hydrolysis of the product yields monobromosuccinic acid, which on treatment with silver oxide and water yields inactive malic acid :

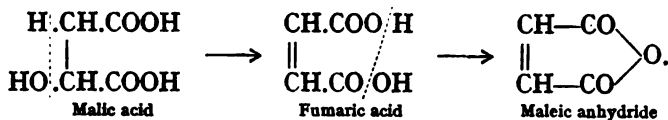


This acid, which melts at 130° , is identical with a mixture of equal quantities of *d*. malic acid and *l*. malic acid.

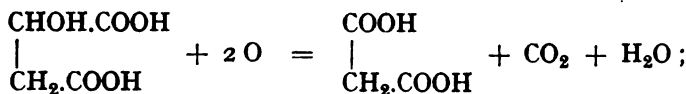
The reactions of the malic acids resemble those of other hydroxyacids. Thus on treatment with phosphorus pentachloride, malic acid is converted into chlorosuccinyl chloride :



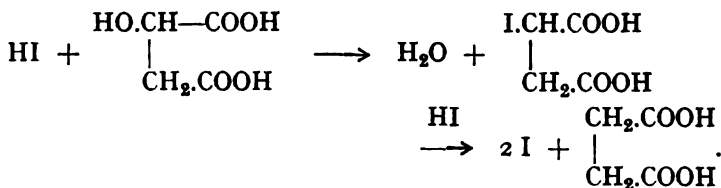
On heating alone, it loses water, forming, like hydracrylic acid, not a lactide or lactone, but an unsaturated acid, *fumaric acid*, which at once loses water, yielding maleic anhydride (p. 265) :



On oxidation it yields malonic acid (p. 187) :



on reduction, by heating with hydriodic acid it is converted into succinic acid :

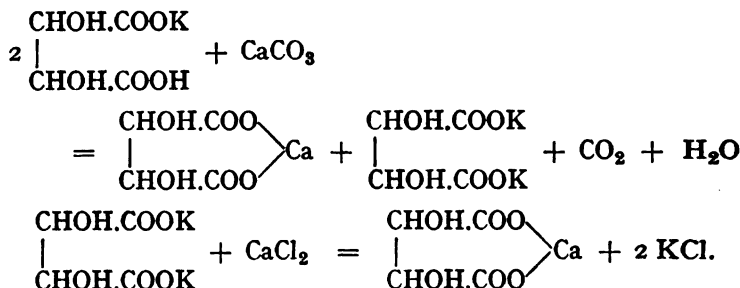


Tartaric acid, dihydroxysuccinic acid :



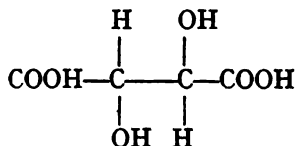
has been known for a long time. Its potassium hydrogen salt $\text{COOH}.\text{CHOH}.\text{CHOH}.\text{COOK}$ is the principal constituent of the *tartar* or *argol* which separates during the fermentation of grape juice in the manufacture of wines. This material forms the chief source for the preparation of tartaric acid ; a hot aqueous extract of crude tartar deposits on cooling pure crystalline potassium hydrogen tartrate, known as "cream of tartar." On adding calcium carbonate to a solution of tartar, insoluble calcium tartrate is thrown out, and soluble potassium tartrate

remains in solution, which, on treatment with calcium chloride, yields a further precipitate of calcium tartrate :



This precipitate can be decomposed with sulphuric acid and the calcium sulphate removed. The solution, on concentration, deposits crystals of tartaric acid, a crystalline solid which melts at 169° .

Consideration of the structural formula :



will make clear the fact that tartaric acid has two asymmetric carbon atoms, to the four valencies of each of which are attached the four different atoms or groups, namely, —H , —OH , —COOH and —CHOH.COOH . The existence of optically active tartaric acids is thus to be expected, and this is in fact observed, for the tartaric acid obtained from tartar is found to rotate the plane of polarised light to the right. A laevorotatory tartaric acid, corresponding in every way with ordinary *dextro* tartaric acid, is also known. Its modes of preparation will be discussed later.

A third—optically inactive—acid, the chemical properties of which are expressed by the formula :



is known. This is called **racemic acid**. It differs from ordinary tartaric acid in many ways; it crystallises with water of crystallisation, which it loses at 110° , and then melts at 204° . Its solubility in water is markedly less than that of *d*-tartaric acid, and its salts differ similarly from the corresponding *d*-tartrates. It occurs as a by-product in the manufacture of tartaric acid from tartar. It is also produced by boiling sodium tartrate with a concentrated solution of sodium hydroxide.

An exhaustive study of the relations between tartaric acid and racemic acid was made by Pasteur in 1860, and in this historic research he laid the foundations of the important branch of chemistry known as *stereochemistry*.

While examining the crystalline form of a number of tartrates, he was struck by the fact that they all possessed an unsymmetrical shape, in that small planes appeared on two corners, as if the corner had been chipped off (Fig. 9). Such a plane is termed a *hemihedral* face; the possession of such a face is termed "hemihedrism."

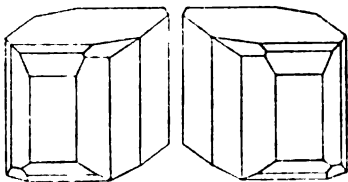


FIG. 9.

The salts of racemic acid, on the other hand, were symmetrical; the hemihedral face at the corner was absent. Now, during the preparation of some crystals of sodium ammonium racemate, he allowed a solution of this salt to evaporate spontaneously at the room-temperature (below 28°), and on examination of the resulting crystals found that hemihedral faces were present, but that the crystals differed from tartrates in that in some of them the hemihedral faces were on one side of the crystal, in some of them on the other side. These two kinds of crystals he separated mechanically, selecting each crystal from the mass with a forceps, and found that the one form was absolutely identical with sodium ammonium tartrate, rotating in aqueous solution to the right, the other form consisting of a salt identical with sodium ammonium tartrate except that it was rotated to the left.

This process is termed the *resolution* of racemic acid into *dextro*-tartaric acid and *laevo*-tartaric acid. It should here be pointed out that racemic acid is not strictly a mixture of the two optical isomers, but a loose chemical compound, and many of its properties are entirely distinct from those of its components. Such an optically inactive substance, a compound of two optically active isomers, of whatever chemical nature, is known as a racemic substance; the general term being borrowed from this particular case.

It is to Pasteur that we owe the discovery of the general method by which racemic compounds can be resolved into their optically active isomers. Many substances occurring in nature are optically active, and are, in fact, pure optical isomers, by which we mean that no trace of racemic compound is present in the active substance. Such compounds are the alkaloids quinine, cinchonine, brucine, strychnine, and some others. Now, if we prepare a salt of an active base, such as quinine, with a racemic acid, we obtain thereby a mixture of salts which are not optical antipodes.¹ Quinine is laevorotatory, so that the mixture consists of *d*.acid-*l*.base and *l*.acid-*l*.base; these salts, not being optical antipodes, differ in chemical and physical characteristics. The probability, therefore, is that their solubilities are different, so that they can be completely separated by fractional crystallisation.

Pasteur was by this means able to resolve racemic acid into *dextro*- and *laevo*-tartaric acids—a process far less tedious and more generally applicable than the mechanical separation of crystals. Racemic bases may similarly be resolved by fractional crystallisation of their salts with optically active acids. Thus if we employ a dextrorotatory acid, the salts *d*.acid-*d*.base and *d*.acid-*l*.base must be separated. The pure active base or acid, thus obtained as a salt, can be liberated by treatment with acid or alkali in the usual manner.

Another method by which Pasteur was able to obtain active compounds from racemic substances was to allow blue mould

¹ The *dextro* and *laevo* varieties of the same compound are often referred to as "optical antipodes."

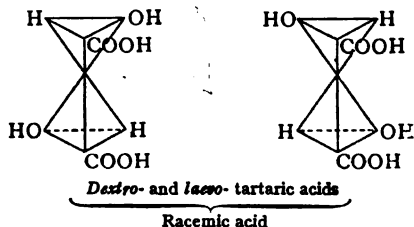
(*penicillium glaucum*) to grow in a solution of a racemic compound. This method has already been mentioned in the case of active amyl alcohol (p. 124), but we may recapitulate by a description of the process as Pasteur applied it to sodium ammonium racemate. To a solution of this salt he added a small quantity of albumen solution, and inoculated the mixture with *penicillium glaucum*. Fermentation took place, and the solution gradually acquired a decided laevorotation. When this had reached a maximum, he precipitated the tartaric acid as its calcium salt, from which he was able to prepare pure *l*-tartaric acid. The mould thus destroys the *dextro* variety, leaving the *laevo* variety almost untouched. This process has been found applicable to the resolution of a large number of racemic compounds, but is not generally employed, since it involves destruction of one-half of the material.

When optically active substances are heated alone or in presence of water, acids, alkalies, or other bodies which act as catalysts, the inactive racemic forms are often produced. This is known as *racemisation*. By its aid Pasteur was able to prepare *l*-tartaric acid from *d*-tartaric acid; namely, by racemisation and subsequent resolution of the racemic acid.

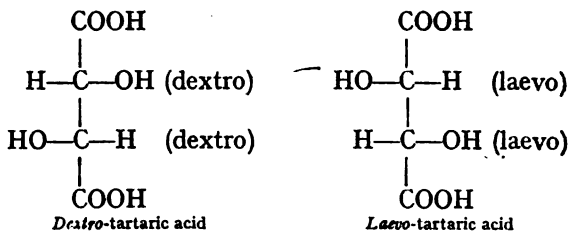
It has just been noted that active tartaric acid is racemised by heat; with some active compounds, however, racemisation proceeds so readily that they lose their activity spontaneously.

We have seen that compounds containing an asymmetric carbon atom, such as lactic acid or malic acid, can occur in three varieties: the *dextro*, *laevo*, and *racemic* forms. Tartaric acid contains two asymmetric carbon atoms, and here the matter is more complicated. The system around each carbon atom can have its own rotatory effect, and the rotation of the entire molecule is the additive effect of the two. In *dextro*-tartaric acid both centres of asymmetry tend to rotate the plane of polarised light to the right; in the *laevo* acid they both tend to rotate to the left; while racemic acid is a loose compound of the two antipodes. This is more clearly shown by tetrahedral

models, in which it is seen that the two acids are true non-superposable mirror-images of each other :



There is a convention by which we formulate this idea :



The hydrogen atoms and hydroxyl groups are arbitrarily placed on one or the other sides of the molecule, to indicate whether the grouping is dextrorotatory or laevorotatory.

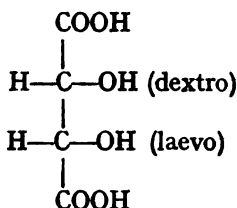
Mesotartaric acid. There exists yet a fourth tartaric acid, called mesotartaric acid. This occurs together with racemic acid when *d*-tartaric acid is racemised by heating with a 40 per cent. solution of caustic potash. It is separated from the racemic acid by fractional crystallisation of the potassium hydrogen salts of the mixed acids, this salt of mesotartaric acid being extremely soluble in water. The free acid crystallises with one molecule of water ; the anhydrous substance melts at 140°.

Mesotartaric acid is optically inactive, but cannot be resolved into active components. It is, moreover, monomolecular. These two facts indicate that it is not a second racemic variety of tartaric acid, but an isomer in which one-half of the molecule tends to rotate to the right, the

other half to the left. Its constitution as shown by tetrahedral models, is :

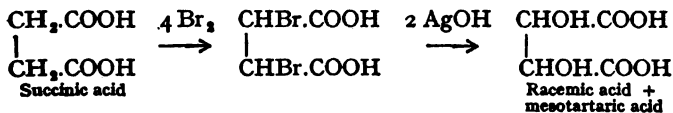


It will be noticed that the one half of the molecule is the mirror-image of the other half. This is expressed by the convention :



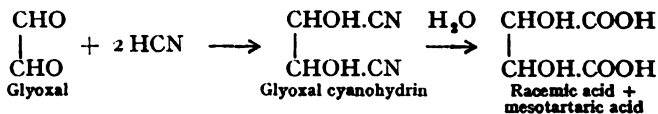
Mesotartaric acid is said to be an *internally compensated* compound ; racemic acid is termed *externally compensated*. The spatial arrangement of the various asymmetric carbon atoms is termed the *configuration* of the molecule.

A mixture of racemic acid and mesotartaric acid is formed by the action of silver oxide and water upon the symmetrical dibromosuccinic acid produced by the bromination of succinic acid :

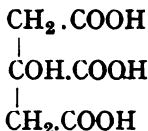


It is highly probable that the conditions which obtain in the dibromosuccinic acids are similar to those in the tartaric acids ; so that the mixture of racemic acid and mesotartaric acids corresponds with a mixture of racemic dibromosuccinic and *meso*-dibromosuccinic acids. It may here be noted that in the ordinary operations by which substances are synthesised, optically active compounds are never produced.

The same mixture of acids is formed by treating glyoxal (p. 129) with hydrogen cyanide and hydrolysing the resulting cyanohydrin :



Citric acid

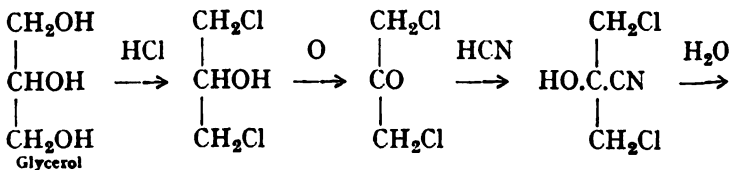


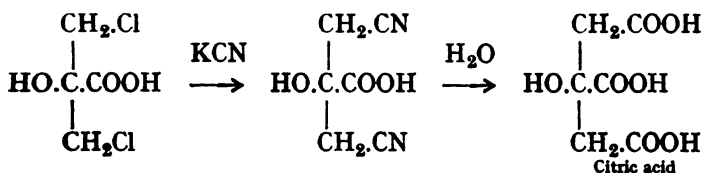
is contained in many fruits, being manufactured from the juice of the lemon, from which its name is derived.

The juice of unripe lemons, which contains some 7 per cent. of citric acid, is boiled and neutralised while hot with calcium hydroxide, whereby the calcium salt, which is insoluble in hot water, is thrown out. This is filtered off, decomposed with dilute sulphuric acid, and the filtered solution concentrated *in vacuo*, when the citric acid separates as a colourless solid crystallising with one molecule of water. Citric acid is also formed in considerable quantity by the fermentation of sugar solutions under the agency of a certain mould (*Citromyces*).

Hydrated citric acid melts at 100°; the anhydrous acid, prepared by heating to 130°, melts at 153°.

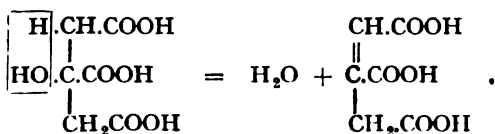
Citric acid has been synthesised by the following series of steps: glycerol (p. 130), on treatment with hydrogen chloride, yields α -dichlorohydrin (p. 131); this, on oxidation, yields symmetrical dichloroacetone; this combines with hydrogen cyanide, and the product yields α -hydroxy- β,β' -dichloroisobutyric acid on hydrolysis; the potassium salt of this reacts with potassium cyanide, forming a dinitrile which yields citric acid on hydrolysis:





Citric acid contains no asymmetric carbon atom; it is optically inactive and cannot be resolved into optically active constituents.

On heating to 175° it loses water, yielding the unsaturated *aconitic acid*, a reaction recalling the behaviour of malic acid on heating:



CHAPTER XIX

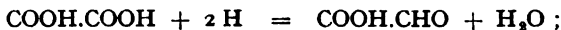
ALDEHYDIC AND KETONIC ACIDS

THE only aldehydic acid which we need consider is **glyoxylic acid** CHO.COOH .

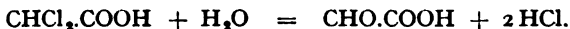
It is formed by the general methods for preparing aldehydes—by oxidation of glycollic acid :



by reduction of oxalic acid by means of sodium amalgam :



or by prolonged heating of dichloroacetic acid with water :

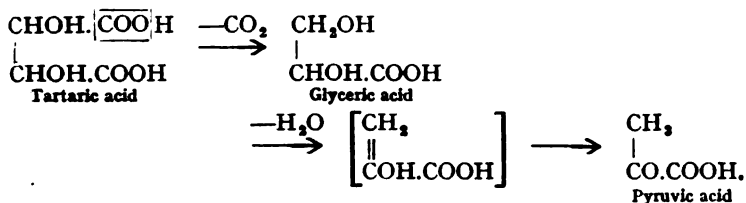


Glyoxylic acid and most of its salts crystallise with one molecule of water, as for instance, $\text{CHO.COOH.H}_2\text{O}$, $\text{CHO.COONa.H}_2\text{O}$. This molecule of water is regarded as "water of constitution," that is to say, hydrated glycollic acid is *dihydroxyacetic acid* $\text{CH(OH)}_2\text{.COOH}$, the aldehydic group being hydrated as in chloral hydrate (p. 151).

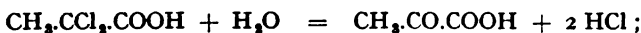
Glyoxylic acid possesses the general properties of aldehydes : it readily reduces mild oxidising agents, such as ammoniacal silver nitrate ; forms a double compound with sodium hydrogen sulphite (p. 143) ; yields an oxime (p. 144) with hydroxylamine, and so on. On boiling with concentrated potassium hydroxide solution it undergoes an intermolecular change analogous to that of form-aldehyde under the same conditions (p. 148), whereby glycollic acid and oxalic acid are formed :



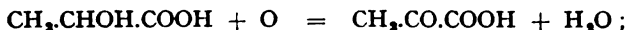
The simplest ketonic acid is **pyruvic acid** $\text{CH}_3\text{.CO.COOH}$. This is produced by heating tartaric acid or glyceric acid. The reaction may be supposed to follow the course :



Other methods of preparation are: by prolonged heating of α - α -dichloropropionic acid with water:



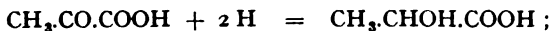
by oxidation of lactic acid:



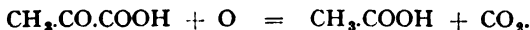
and by treatment of acetyl chloride with potassium cyanide, with subsequent hydrolysis of the resulting acetyl cyanide:



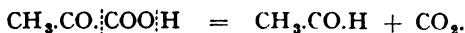
Pyruvic acid is a colourless substance which melts at 9° and boils with decomposition at 165° . It gives the reaction of a ketone: that is to say, it forms an addition-product with sodium hydrogen sulphite, it yields an oxime with hydroxylamine and a phenylhydrazone with phenylhydrazine. On reduction it is converted into lactic acid:



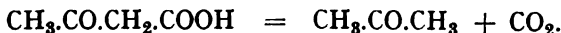
on oxidation it yields acetic acid:



On heating to 150° with dilute sulphuric acid it loses carbon dioxide, acetaldehyde being produced:

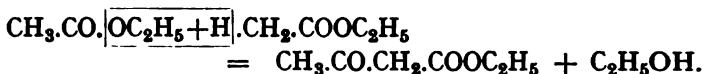


More important is **acetoacetic acid** $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{COOH}$. This acid cannot be isolated in a pure state, since it rapidly decomposes, yielding acetone and carbon dioxide:

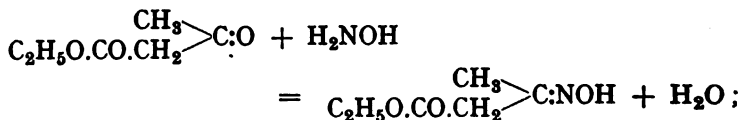


The esters of acetoacetic acid, however, are stable, and can be isolated. **Ethyl acetoacetate** $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$, often known by the more general term *acetoacetic ester*, is prepared by treating ethyl acetate with sodium ethoxide or metallic sodium.

The reaction is a complicated one ; in essence, one molecule of ethyl alcohol is split off between two molecules of ethyl acetate :



Ethyl acetoacetate is a colourless liquid which boils at 180° . It behaves as a ketone in yielding an oxime with hydroxylamine :



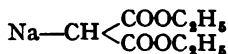
in forming an addition-product with sodium hydrogen sulphite ; and in other ways.

The most notable property of esters of acetoacetic acid is one common to substances containing the grouping :

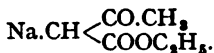


namely, that of yielding metallic derivatives. It will be recalled that esters of malonic acid, such as ethyl malonate (p. 188), also possess this property.

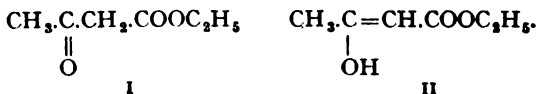
The sodium derivative of ethyl malonate was formulated thus :



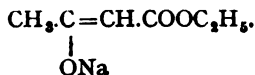
and in a similar way, the sodium derivative of ethyl acetoacetate may be written :



Nevertheless, the fact that the existence of stable compounds containing a sodium atom directly attached to a carbon atom is unusual, would lead us to look for some structure in which a hydroxyl group is present, the hydrogen atom of which would be replaced by sodium. This can be done by assuming a hydrogen atom to wander from carbon to oxygen, with consequent shifting of the double bond :



The sodium salt could then be written :



Ethyl acetoacetate, prepared by the method outlined above is an equilibrium mixture of the two forms (I) and (II) ; the ketonic form (I) can be isolated by cooling a solution of the ester in dry ether to -78° , when crystals of the pure ketonic ester are deposited. The hydroxylic or " enolic " form (II) can be prepared in a pure state by decomposing the sodium salt with hydrogen chloride in dry ether at -78° . Both forms, on standing, revert to the equilibrium mixture, which contains about 7.7 per cent. of the enolic form (II).

This phenomenon—that of a chemical individual existing in two distinct but interchangeable structural forms—is known as *tautomerism* or *desmotropy*. It is usually associated, as in this case, with the migration of a hydrogen atom from one element to another. Strictly speaking, the term *tautomeric* is applied to substances in which only the equilibrium mixture of the structural isomers is known, the word *desmotropic* is employed in cases when the isomers have been shown to be capable of independent existence.

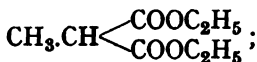
The sodium derivative of ethyl acetoacetate is, from what has gone before, most conveniently formulated as a derivative of the enolic form :



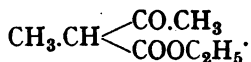
By analogy, therefore, we may formulate the sodium salt of malonic ester thus :



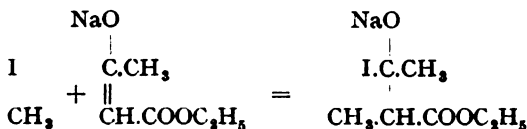
On treating ethyl sodiomalonate with methyl iodide, we obtain ethyl methyl-malonate (p. 189) :



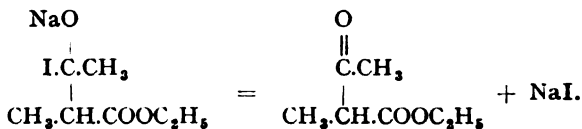
similarly, the sodium derivative of ethyl acetoacetate yields ethyl methyl-acetoacetate on treatment with methyl iodide :



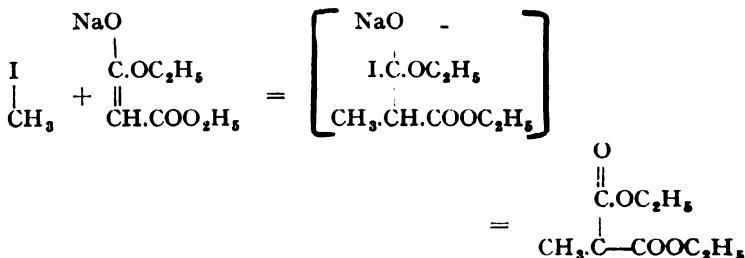
The mechanism by which this reaction occurs is **uncertain**. It is supposed that addition first takes place in the sense :



and that sodium iodide is at once eliminated :

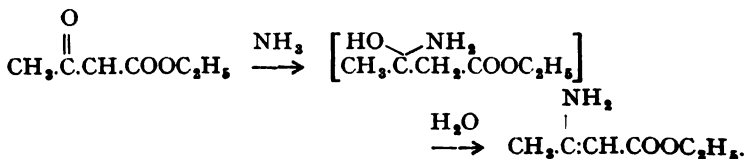


The reaction would follow a similar course in the case of malonic ester :



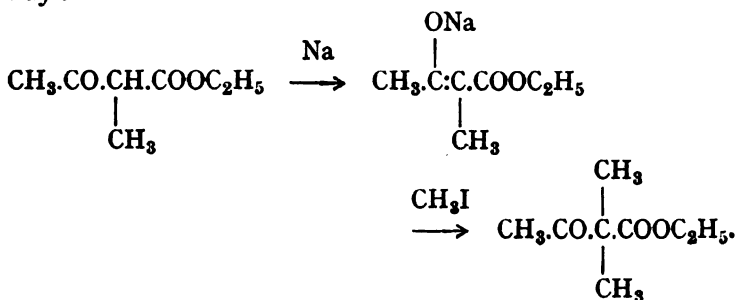
This explanation may, at first sight, appear lame, but it must be remembered that the whole problem is without parallel in the reactions hitherto discussed.

On treatment with ammonia, ethyl acetoacetate is converted into ethyl β -aminocrotonate, an unstable addition-product being formed as an intermediate stage :



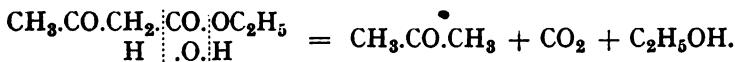
This compound unquestionably exists in the form of an amino derivative of crotonic acid, corresponding to the enolic form of the acetoacetic ester. On treatment with dilute acids it regenerates ammonia and ethyl acetoacetate.

The second hydrogen atom in the methylene group of ethyl acetoacetate can be replaced by an alkyl group in the same way :

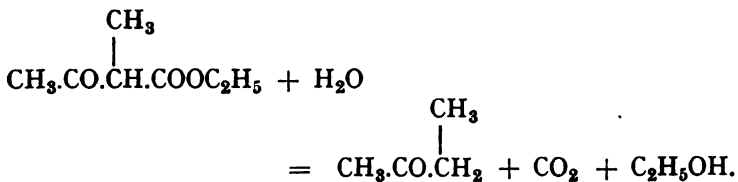


The resulting dialkyl derivative does not form a sodium salt, since a sodium atom is incapable of replacing a methyl group. Enolic forms of such derivatives likewise do not exist.

Ethyl acetoacetate may be hydrolysed in different ways. If it be heated with dilute aqueous acids, alcohol and carbon dioxide are split off, acetone being produced :



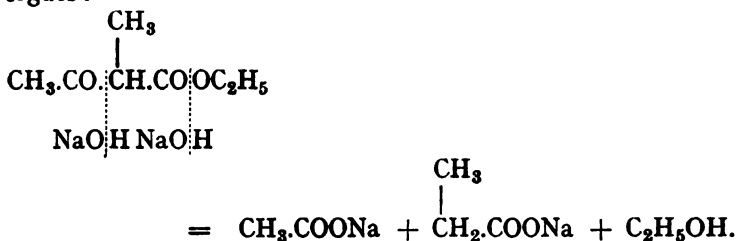
The alkyl derivatives, prepared by the interaction of the sodium salt of ethyl acetoacetate and alkyl halides, undergo a similar hydrolysis :



By selecting a suitable alkyl halide, more complex ketones can thus be synthesised. This reaction is known as the "ketonic hydrolysis" of acetoacetic esters.

If, on the other hand, ethyl acetoacetate or its alkyl derivatives be heated with concentrated aqueous alkali, hydrolysis

follows a different course, yielding acetic acid and its homologues :



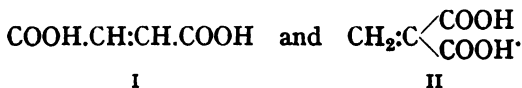
This reaction is an example of the "acid hydrolysis" of acetoacetic esters.

It can readily be understood that ethyl acetoacetate, like ethyl malonate, has proved extremely valuable in synthetical organic chemistry.

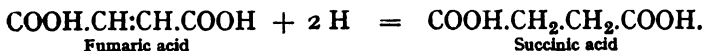
CHAPTER XX

MALEIC AND FUMARIC ACIDS

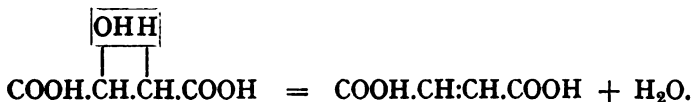
WHEN malic acid (p. 247) is submitted to dry distillation, the chief products are an acid called **fumaric acid** and an acid anhydride called **maleic anhydride**. Fumaric acid is an unsaturated dicarboxylic acid derived from ethylene; its composition may be expressed by $C_2H_2(COOH)_2$. The only two possible structural formulæ are :



On reduction, succinic acid is produced; this shows that all four carbon atoms are in a straight chain. Fumaric acid must therefore be associated with formula I :



The formation of fumaric acid from malic acid is thus readily explained :



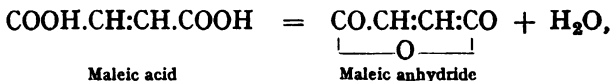
Now maleic anhydride, the second product of dry distillation of malic acid, reacts with alkali, forming a salt from which **maleic acid**, a substance entirely distinct from fumaric acid, can be prepared by the usual methods. Fumaric acid sublimes

at about 200° , but under pressure melts at 286° . Maleic acid, on the other hand, melts at 130° . Other properties, such as solubility, also differ markedly; maleic acid is far more soluble in water than fumaric acid; barium maleate is insoluble, barium fumarate is soluble in water, and so on. There is thus no question of the difference in identity of the two acids.

Maleic acid is also an unsaturated dicarboxylic acid $C_2H_2(COOH)_2$, and is therefore isomeric with fumaric acid. Yet, on reduction, it also yields succinic acid, and must likewise be represented by the formula $COOH.CH:CH.COOH$.

Here we have a new class of isomerism; both acids are optically inactive, but as they contain no asymmetric atom, the difference cannot be similar to that between racemic acid and mesotartaric acid. Moreover, all attempts to resolve either fumaric acid or maleic acid into optically active components have failed.

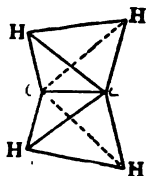
A remarkable feature is the ease with which the isomers can be converted one into the other:—maleic acid, on heating alone or in presence of a trace of iodine or hydrogen bromide, is converted into fumaric acid; both maleic acid and fumaric acid, on heating to a higher temperature, lose water and form *the same* anhydride—maleic anhydride, from which maleic acid can be prepared:



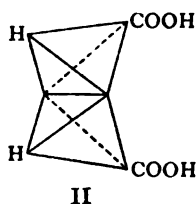
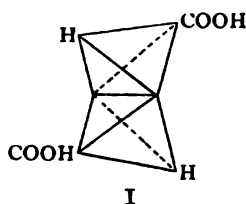
Anhydride formation proceeds much more readily with maleic acid than with fumaric acid; the end-product, as stated, is the same in both cases. No anhydride yielding fumaric acid on hydrolysis is known.

The theory by which this isomerism is explained is due to Wislicenus, though it had been adumbrated some years before by van't Hoff. It involves the application of the idea of the "double bond" in ethylenic compounds to the tetrahedral conception of the valencies of the carbon atom. In ethylene, the two carbon atoms are united by two of the valencies of each

atom ; this we may picture by tetrahedrons united along one edge :



In maleic acid and fumaric acid, one of the hydrogen atoms attached to each carbon atom is replaced by a carboxyl group. It is obvious, from the spatial diagram, that this can be done in two ways, so that the carboxyl groups lie either on opposite sides of the molecule (I) or on the same side of it (II) :

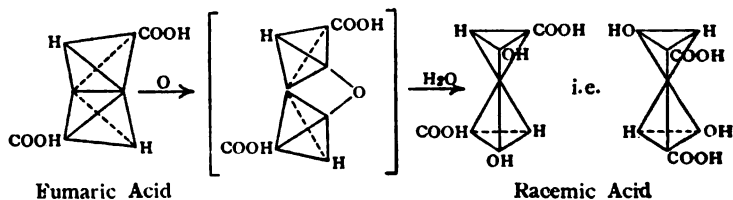


Such, according to the theory of Wislicenus, is the nature of the isomerism of fumaric acid and maleic acid. It is termed *geometrical isomerism*, and has been found to occur in a large number of similar cases.

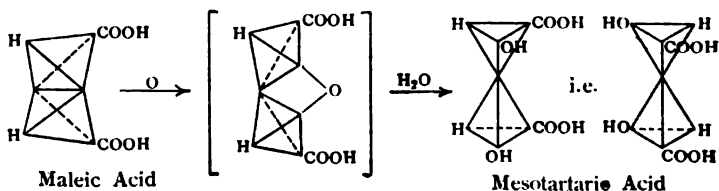
Formula I is associated with fumaric acid, formula II with maleic acid, for a variety of reasons. Since fumaric acid is obtained by warming maleic acid, whilst the reverse change does not take place, fumaric acid is considered to be the more stable form ; and as (I) is the more symmetrical structure, it is attributed to fumaric acid, as symmetry of structure is assumed to go hand-in-hand with stability. A more conclusive reason for this view is that the anhydride of maleic acid alone is known. In (II) the carboxyl groups are nearer together in space than in (I), and it seems reasonable to conclude that when the carboxyl groups are closer together the internal anhydride would be more readily formed.

Form (I) is termed the *trans* or "fumaroid" form; (II) the *cis* or "maleinoid" form.

A further example of the type of reason which leads to the "trans" formulation of fumaric acid and the "cis" formulation of maleic acid is the behaviour of these acids on gentle oxidation. Fumaric acid yields racemic acid (p. 251):



Maleic acid yields mesotartaric acid (p. 254):

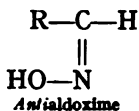
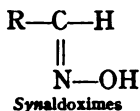


These reactions show the interdependence of the theories of geometrical isomerism and optical isomerism, and their dependence upon the spatial conception of the valencies of the carbon atom. It is customary to differentiate fumaric acid and maleic acid—as indeed all geometrical isomers—by the scheme:

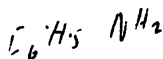
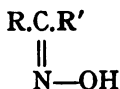


It may here be pointed out that a similar type of geometrical isomerism has been observed in the oximes (p. 144). On treating certain aldehydes with hydroxylamine, it has been

found that two isomeric aldoximes can be obtained ; to these the formulæ :



are respectively assigned. With ketones, stereoisomeric oximes have been observed only when the radicles attached to the carbonyl group are *different* from each other :



CHAPTER XXI

CARBOHYDRATES

CARBOHYDRATES may be defined as compounds of the general formula $C_mH_{2n}O_n$, in which alcoholic hydroxyl groups and aldehydic or ketonic carbonyl groups are present. The name "carbohydrate" is derived from the fact that in empirical composition these substances consist of carbon in combination with oxygen and hydrogen in the proportion of $C_m(H_2O)_n$, and in the early days of chemistry they were, by a stretch of the imagination, regarded as hydrates of the element carbon. The simplest "carbohydrates" under this definition are thus formaldehyde CH_2O , and glycollic aldehyde $CH_2OH.CHO$ —the aldehyde corresponding to glycollic acid (p. 241). Carbohydrates containing three carbon atoms can contain either an aldehydic or a ketonic carbonyl group :—these are the aldehyde of glyceric acid (p. 247) and dihydroxyacetone :



Glyceric aldehyde



Dihydroxyacetone

The nomenclature of the carbohydrates involves the use of the suffix *-ose* ; those containing aldehydic carbonyl groups are termed *aldoses*, those containing ketonic carbonyl groups are called *ketoses*. As a general rule carbohydrates are normal, or straight-chain, compounds ; the number of carbon atoms in the chain is indicated by inserting the Greek numerals. Glycollic aldehyde is thus an *aldodiose*, glyceric aldehyde an *aldotriose*, whilst dihydroxyacetone is a *ketotriose*.

The simpler carbohydrates are classified under the general

heading of "sugars," these being subdivided into *monosaccharides*, *disaccharides*, *trisaccharides*, and so on. The explanation of this subdivision will appear later in the text. The majority of the carbohydrates are optically active.

MONOSACCHARIDES

This term includes all carbohydrates of the general formulæ $H.[CHOH]_n.CH:O$ and $H.[CHOH]_n.CO.CH_2OH$. The only important classes under this heading are the pentoses and the hexoses—that is to say, sugars containing respectively five and six carbon atoms in the molecule.

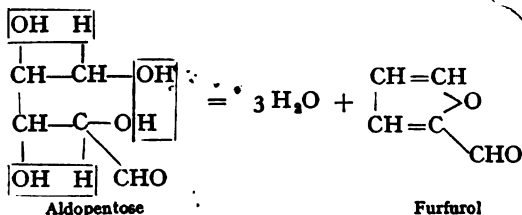
Monosaccharides as a class are expressible by the general formula $C_nH_{2n}O_n$,—in other words, the number of oxygen atoms in the molecule is equal to the number of carbon atoms. Monosaccharides contain only one carbonyl group in the molecule, the remaining atoms of combined oxygen existing in the form of alcoholic hydroxyl groups. A further general feature is that carbohydrates as a class contain no carbon atoms to which oxygen is not directly united.

In physical properties the monosaccharides are sweet-tasting, crystalline, colourless solids, which are, as a rule, very soluble in water, less so in alcohol, and insoluble in ether. In chemical properties they are characterised by the ease with which they may be oxidised and dehydrated. They possess the general chemical properties attributable to carbonyl compounds (combination with hydrogen cyanide, reaction with hydroxylamine and phenylhydrazine, etc.) and to hydroxylic compounds (esterification, etherification, etc.).

Pentoses occur in nature, or are readily obtained from some natural products. Such are **arabinose** $CH_2OH.CHOH.CHOH.CHOH.CHO$, which is produced by boiling gum-arabic with dilute sulphuric acid, and **xylose**, which is stereoisomeric with arabinose and resembles it closely in chemical properties, and which is obtained by boiling certain woody fibrous materials, such as straw or jute, with dilute sulphuric acid.

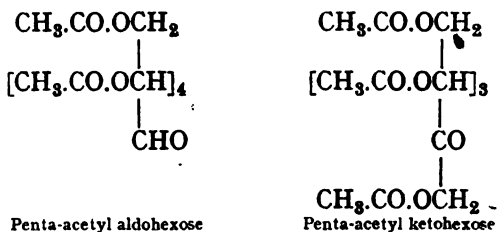
Pentoses as a class may be distinguished from the hexoses by the fact that they are not fermented by yeast. Characteristic of

aldopentoses is the formation of *furfural*—an aldehyde of cyclic structure—on prolonged boiling with dilute mineral acids :



The presence of furfural may be demonstrated by exposing to the vapours a piece of paper moistened with aniline hydrochloride (p. 360) ; this assumes a pink coloration.

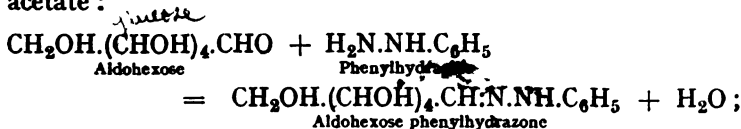
Of greater importance are the **hexoses**, and to these we shall devote our chief attention. In chemical properties they are typical monosaccharides ; they are readily oxidised, and reduce alkaline solutions of cupric salts (Fehling's solution—a mixture of copper sulphate and sodium hydroxide with sodium potassium tartrate, which prevents the precipitation of cupric hydroxide) and ammoniacal solutions of silver salts, yielding respectively cuprous oxide and metallic silver. The presence of five alcoholic hydroxyl groups in hexoses is shown by the formation of penta-acetates on treatment with acetic anhydride :



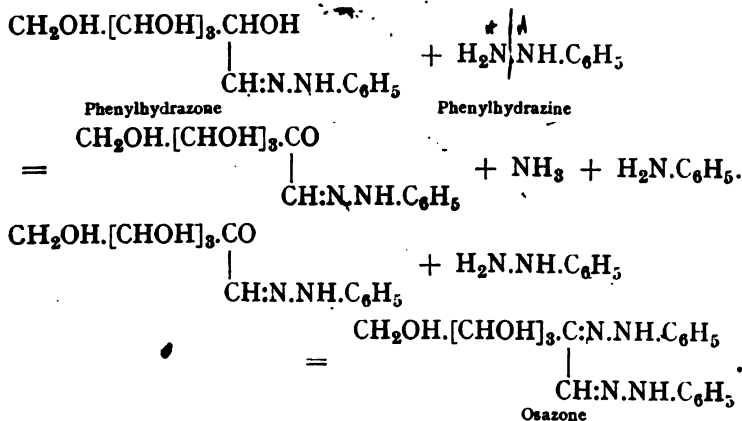
They show their constitution as aldehydes or ketones by the general reactions of carbonyl compounds ; they form addition-products (cyanohydrins, p. 143) with hydrogen cyanide, oximes (p. 144) with hydroxylamine, and phenylhydrazones (p. 144) with phenylhydrazine. On boiling with alkalis they are decomposed, yielding resinous products.

The phenylhydrazones of hexoses are, as a rule, very soluble

in water, and are hence not precipitated on warming a solution of an aldohexose or a ketohexose with phenylhydrazine acetate :



on continued treatment with excess of phenylhydrazine, a second reaction takes place, whereby the phenylhydrazone reduces some of the phenylhydrazine, being converted into a carbonyl compound, which at once reacts with more phenylhydrazine to yield a di-phenylhydrazone or *osazone* (cf. p. 379) :



The osazones thus formed are yellow solids, insoluble in water, which crystallise in characteristic forms, and are for this reason employed for the identification of hexoses.

The majority of the hexoses differ from the pentoses in that they are decomposed by the action of ferments such as yeast. Examples of fermentation of hexoses have already been quoted (pp. 114, 165, 243, 256). The most important physical property of the pentoses and hexoses is that of optical activity. Characteristic of each member of the group is the direction and the amount of the rotation of polarised light by their solutions. It has already been shown, in discussing the tartaric acids

(p. 250), how the differences in the spatial arrangement of the hydrogen atoms and hydroxyl groups can cause differences in chemical and physical properties. In the sugars the same phenomenon occurs, but is rendered far more complicated by the presence of a greater number of —CHOH— groups. In this fact lies the explanation of the existence of so many different isomeric hexoses.

ALDOHEXOSES

Aldohexoses all possess the structural formula



That they are all derived from normal hexane—that is, that the six carbon atoms are arranged in a straight chain—is shown by the fact that they all yield a mixture of secondary normal hexyl iodides :



on heating with hydriodic acid (cf. p. 134).

As above indicated, the cause of isomerism among the various aldohexoses is stereochemical; inspection of the structural formula reveals the fact that all of the four carbon atoms (printed in heavy type) not situated at the end of the chain :



are asymmetric carbon atoms, and can give rise to the type of stereoisomerism exhibited by the tartaric acids. Since there are four asymmetric atoms which can have different spatial relations, or, as they are termed, “configurations,” isomerism is naturally extremely complicated, inasmuch as *dextro*-, *laevo*-, and *meso*-configurations are possible, not to mention the possibility of the existence of racemic isomers (p. 254). In no other branch of organic chemistry has stereochemistry rendered such service as in the domain of sugars. By his researches into the constitution of the sugars, Emil Fischer has been able to predict the existence of, and ultimately synthesise—or prepare from natural products—all the possible aldohexoses—

of which there are no less than sixteen—and assign to each its spatial configuration.

Aldoses give many of the general reactions of aldehydes : for instance, they restore the pink colour to a solution of fuchsine (p. 436) in aqueous sulphurous acid (Schiff's reagent). This reaction serves to distinguish them from the ketoses.

Glucose, also called *grape-sugar* or *dextrose*, is the most important of the aldohexoses. It occurs in nature as the chief constituent of honey, and is present in the juice of grapes and other fruits. It is also present in the urine of diabetic patients. In technical practice it is prepared by the hydrolysis of cane-sugar, starch, or cellulose, by treatment with aqueous mineral acids. So prepared, it is employed in the manufacture of confectionery, preserved fruits, and beer.

Glucose is extremely soluble in water, and separates from a concentrated aqueous solution with one molecule of water of crystallisation. It is also soluble in alcohol, from which it crystallises in the anhydrous condition. It is strongly dextro-rotatory, from which fact the name "dextrose" is derived. The specific rotation $[\alpha]_D^{20}$ as defined on p. 120, is $+ 52.8^\circ$.

The structural formula for glucose, written without regard to its spatial configuration, is :



On reduction it yields a hexahydroxylic alcohol, *d-sorbitol* :



On oxidation it yields at first *gluconic acid* :



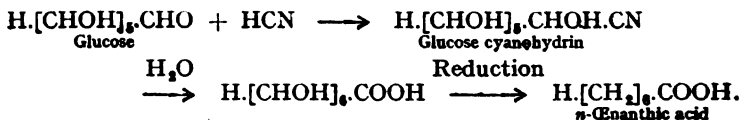
and, on further oxidation, *saccharic acid* :



On powerful oxidation, as with hot concentrated nitric acid it is broken down into oxalic acid (p. 184).

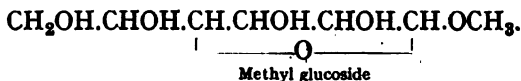
The constitution of glucose has further been demonstrated by adapting the known faculty of carbonyl groups of reacting with

hydrogen cyanide: the series of steps is shown in the following scheme:



This conversion of glucose into normal enanthic acid proves firstly that glucose is a derivative of normal hexane; secondly that the carbonyl group is situated at the end of the carbon chain.

On treatment in methyl-alcoholic solution with gaseous hydrogen chloride, a product is obtained in which a methyl group has replaced a hydrogen atom in the glucose molecule. This is **methyl glucoside**. Inasmuch as only one methyl group has entered the molecule, intramolecular ether-formation has also taken place, resulting in a compound to which the following formula is ascribed:



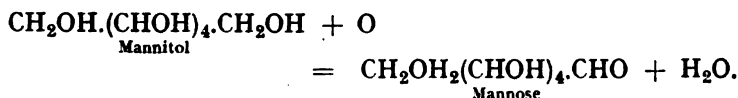
It may thus be regarded in the light of an acetal (p. 146), which class of compound it resembles in many ways, notably by its absence of reducing powers, its failure to react with phenylhydrazine, hydroxylamine, or hydrogen cyanide, and its facility for undergoing hydrolysis on boiling with dilute mineral acids.

Glucosides of hydroxylic compounds other than methyl alcohol are also known; many of these occur in nature (p. 389).

The two chief methods by which glucose can be quantitatively estimated are by observation of rotation and by oxidation. The first method consists in determining the degree of rotation of a solution of glucose in the polarimeter, and from the known specific rotation of glucose calculating the percentage concentration of the solution. The second method involves the use of Fehling's solution or one of its modifications. An alkaline solution of an alkali tartrate has the property of dissolving cupric hydroxide, and this fact is utilised in the preparation of Fehling's solution. Measured volumes of a standard solution of copper sulphate and an approximately standard

solution of sodium hydroxide and sodium potassium tartrate (" Rochelle salt ") are mixed, and the mixture heated to gentle boiling. The glucose solution is then added from a burette to the boiling mixture until the original blue colour of the Fehling's solution just vanishes. The amount of sugar solution necessary to reduce the known quantity of cupric oxide to cuprous oxide must be determined empirically, by standardisation against a glucose solution of known concentration. A variant of Fehling's solution is Pavy's solution, in which the cupric hydroxide is held in solution by ammonia.

Mannose is an aldohexose, stereoisomeric with glucose, which is produced, together with lævulose (p. 278), by the cautious oxidation of the hexahydroxylic alcohol mannitol (p. 134).



It occurs, in a combined form, in certain vegetable products. Its close relation to glucose is shown by the fact that on prolonged treatment with excess of phenylhydrazine it yields the same osazone as glucose (p. 273). Mannose differs from the other hexoses in that its phenylhydrazone $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ is sparingly soluble in water, so that it is formed as a precipitate under the conditions which lead, in the case of the remaining hexoses, to the formation of osazones.

On oxidation it yields *mannonic acid* $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, and *mannosaccharic acid* $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, different from, but stereoisomeric with, gluconic acid and saccharic acid (p. 275) respectively.

Galactose is another stereoisomer of glucose. It is formed, together with glucose, by the hydrolysis of lactose, or milk sugar (p. 281).

With phenylhydrazine it forms a characteristic osazone. On reduction it is converted into the hexahydroxylic alcohol dulcitol, stereoisomeric with mannitol and sorbitol. On oxidation it first yields *galactonic acid*, stereoisomeric with gluconic acid, and then a dicarboxylic acid *mucic acid* $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, which differs from the stereoisomeric saccharic acid in being almost insoluble in water, and in being optically inactive, owing to its possessing a *meso*- (p. 255) configuration.

KETOHEXOSES

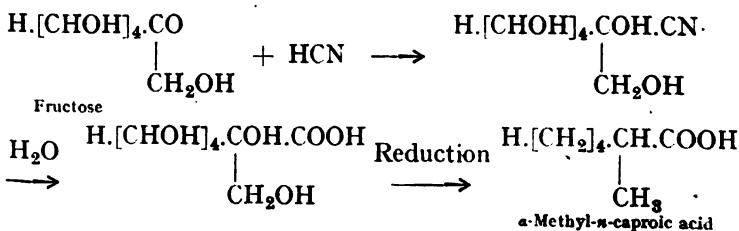
The only member of this class which we need consider is **fructose**, also called *fruit sugar* or *lævulose*. We may here briefly review the chief reasons for considering it a penta-hydroxylic ketone of the formula :



- (1) On reduction with hydriodic acid it yields, like glucose and the other aldohexoses, a mixture of secondary normal hexyl iodides (p. 274), and must therefore likewise be a derivative of normal hexane.
- (2) It does not recolorise Schiff's reagent (p. 275)—a reaction specific to aldehydes.
- (3) It forms a cyanohydrin, an oxime, and a phenylhydraz-one. For these reasons it must be regarded as a ketone.
- (4) It yields a penta-acetate on treatment with acetic anhydride, and must therefore possess five hydroxyl groups.

The reasons for regarding the carbonyl group as situated in the β -position (the second carbon atom in the chain) are as follows :

(5) On careful oxidation it yields glycollic acid $\text{CH}_2\text{OH}.\text{COOH}$ and tri-hydroxyglutaric acid $\text{COOH}.\text{(CHOH)}_3.\text{COOH}$. This in itself is insufficient to establish the position of the carbonyl group, but the following series of changes leaves no doubt (cf. p. 276) :



Fructose is a l vrotatory compound resembling the aldohexoses in general character. It occurs together with glucose in

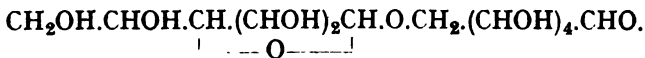
the fruits of many plants, and is formed, together with glucose, by the hydrolysis of cane sugar. It is further formed exclusively by the hydrolysis of inulin, a member of the starch family.

Fructose, although no aldehyde, is oxidised like glucose by Fehling's solution, which can be employed for its estimation. In aqueous solution its specific rotation is $[\alpha]_D^{20} = -90.2^\circ$. On treatment with excess of phenylhydrazine acetate it yields the same osazone as does glucose—a further confirmation of the presence of the carbonyl group in the β -position. It thus possesses a spatial configuration closely akin to that of glucose. On reduction it yields a mixture of approximately equal quantities of mannitol (p. 134) and sorbitol (the product of reduction of glucose).

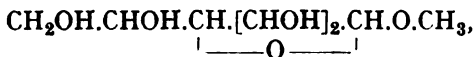
DISACCHARIDES

In describing the chief properties of glucose, mention was made of the class of compounds known as glucosides (p. 276), which in structure and chemical character show a close similarity to the acetals. The important class of sugars, the disaccharides, consists of compounds of two molecules of monosaccharide which are condensed together in the manner of glucosides:—their composition is given by the empirical formula $C_mH_{2m-2}O_{m-1}$, or $2C_nH_{2n}O_n - H_2O$.

There are two distinct ways in which the two molecules of monosaccharides may be linked together. The first is that in which one molecule of hexose functions as a carbonyl compound, and the other as an alcohol. Such are maltose and lactose, which are stereoisomers of the structural formula :



These are analogous to methyl glucoside :



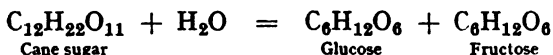
and in addition possess the properties common to aldoses (reduction of Fehling's solution, osazone formation, oxime

Lactose or *milk sugar* $C_{12}H_{22}O_{11} + H_2O$ occurs in milk. It is prepared by precipitating the proteins (curds) by means of acetic acid or rennet, and evaporating the clear filtrate (whey) to dryness. In chemical character it is a true aldehydic disaccharide like maltose. It is not fermented by yeast, but under the action of certain ferments contained in milk it yields lactic acid and butyric acid. Another ferment, known as *lactase*, is capable of inducing alcoholic fermentation—a process which underlies the preparation of the alcoholic beverage koumiss. On hydrolysis with acids it yields a mixture of glucose and galactose.

Lactose is a white crystalline solid, dextrorotatory in aqueous solution, having $[\alpha]_D = +52.5^\circ$. On oxidation with nitric acid, both saccharic acid and mucic acid are produced. It reduces Fehling's solution and forms an osazone.

Cane sugar, also called *saccharose* or *sucrose*, $C_{12}H_{22}O_{11}$ differs, as above stated, from maltose, and lactose in possessing no aldehydic or ketonic properties.

Its constitutional formula has already been given on p. 280. On hydrolysis with aqueous mineral acids it yields a mixture of equal parts of glucose and fructose :

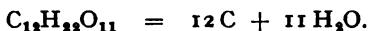


It does not reduce Fehling's solution ; it fails to react with phenylhydrazine, with hydroxylamine, and with hydrogen cyanide ; it is not decomposed by boiling with alkalis ; and it is not attacked by the *zymase* (p. 114) of yeast. By the action, however, of another ferment, *invertase*, it is converted into glucose and fructose.

Cane sugar is strongly dextrorotatory, having $[\alpha]_D = +66.5^\circ$ in water. After hydrolysis with mineral acids, a solution of cane sugar rotates to the left, owing to the fact that fructose has a greater lævorotatory power than the dextrorotatory power of glucose ; this hydrolysis is therefore termed *inversion*, and the resultant equimolecular mixture of glucose and fructose is known as *invert sugar*. The principal method of estimating cane sugar quantitatively consists in determining the rotation

of the sugar solution under examination. Cane sugar may also be estimated by "inverting" the sugar by warming with hydrochloric acid, neutralising, and, after diluting to a definite volume, titrating against boiling Fehling's solution.

Cane sugar is very soluble in water, and crystallises from a concentrated solution in colourless prisms melting at 160° . On heating just above its melting-point it turns brown, being converted into an amorphous substance called *caramel*. On heating to a higher temperature it is carbonised, forming water and a very pure form of charcoal :



This reaction is, however, by no means quantitative ; a number of volatile organic substances, such as acetic acid, acetone, and more complex products, are simultaneously evolved. Cane sugar is also carbonised on warming with concentrated sulphuric acid, a small quantity of sulphur dioxide being liberated by the reducing action of the decomposition products upon the sulphuric acid. On treatment with strong nitric acid, it is oxidised to oxalic acid.

Cane sugar forms loose compounds with alkaline earths, such as the oxides of calcium, strontium or barium. Use is made of the sparing solubility of the compound $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO}$ in the manufacture of sugar.

Cane sugar occurs widely throughout the vegetable world. Its principal sources are the sugar-cane of the West Indies, the sugar-beet of Europe, and the sugar-maple of North America. In the sugar-cane process, the juice of the cane is first treated with lime in order to precipitate the proteins and acid substances. The clear liquor is then concentrated until the "brown sugar" crystallises out. The mother-liquor consists of molasses.

More important is the sugar-beet industry, which provides by far the greatest part of the world's supply. The roots are finely divided and treated with warm water ; the solution thus obtained contains besides cane sugar a trisaccharide called raffinose (see below), phosphoric acid and phosphates, some organic acids such as oxalic and citric acids, some albuminous substances (proteins) and a nitrogenous compound called betaine (p. 291). In order to remove these impurities, the solution is heated, whereby the proteins are coagulated, and on addition of lime, the insoluble calcium salts of the phosphoric and organic acids are precipitated. The remainder of the lime enters into loose combination with a portion of the sugar, and the so-called *calcium sucrosate* or *saccharosate* must therefore be decomposed by passing carbon dioxide into the liquid until the solution is only faintly alkaline. After filtration, the solution is concentrated under diminished pressure in

steam-heated vacuum pans, until the sugar begins to crystallise. After cooling, the crystalline sugar is centrifugally separated.

The mother-liquor, or molasses, still contains considerable quantities of sugar which is prevented from crystallisation by the presence of impurities. In order to extract this, an excess of a hot saturated solution of strontium hydroxide is added, whereby the compound $C_{12}H_{22}O_{11} \cdot SrO$, called *strontium sucrosate*, is precipitated from the concentrated solution. This is separated, dissolved in water, and decomposed by carbon dioxide. The resulting sugar solution is filtered free of strontium carbonate, and concentrated until the sugar crystallises.

The crystallised sugar obtained as above described still contains considerable impurities. In the case of sugar from the sugar-cane, these impurities are not harmful, so that the raw brown sugar from cane can be employed for food. In the case of the raw beet sugar, on the other hand, the impurities are of an unwholesome nature, and must be removed by a process of refining. This consists principally of recrystallisation from water, after passing the solution over animal charcoal, which absorbs the coloured impurities. The syrupy residues, from which no further sugar can be obtained by crystallisation, are worked up for betaine (from which trimethylamine and methyl chloride are technically produced), and fermented for the production of ethyl alcohol.

TRISACCHARIDES.

The only trisaccharide of any importance is **raffinose**,



which is present in the sugar-beet. On hydrolysis it breaks down at first into fructose and a disaccharide called *melibiose*; this latter, on further hydrolysis, yields a mixture of glucose and galactose. Raffinose is therefore a condensation product of fructose, glucose and galactose. It is dextrorotatory, and, like cane sugar, possesses no aldehydic or ketonic properties; it is stable, for instance, towards Fehling's solution. Melibiose, on the other hand, is a disaccharide possessing distinct aldehydic properties.

HIGHER CARBOHYDRATES

Under this heading fall the starches, the dextrans and the celluloses. These are all complicated condensation-products of hexoses, and very little is accurately known as to their chemical constitution.

Starch $(C_6H_{10}O_5)_n$ is present in all vegetable life, and it

is considered to be one of the first products formed by the plant on assimilating carbon dioxide, being the form in which the nutriment is stored by the organism.

It is a white amorphous substance, existing in the form of grains in the vegetable cells. The shape and general appearance of the starch grains is characteristic for the different plants, and from microscopical examination of a sample of starch it is generally possible to determine its source.

Its mode of preparation is simple: the raw material (chiefly potato, maize, wheat, rice, and similar cereals) is finely ground, in order to break up the cells, and the resulting mass is washed in a straining cloth in a stream of water. The starch grains pass through the meshes, leaving behind the cell membranes together with protein material, and these are allowed to settle to the bottom of the liquid, whereupon they are removed and carefully dried.

If starch, in the form of starch grains, which are insoluble in cold water, be heated with water, the grains burst, and a portion enters into solution. Such a mixture, called *starch-paste*, can be separated into water-soluble and water-insoluble components. On standing with concentrated hydrochloric acid starch grains are converted into a so-called *soluble starch*, which dissolves in hot water.

Characteristic of starch-paste and soluble starch is the blue colour which is developed in their solutions by the addition of a trace of iodine. This colour disappears on warming, but reappears on cooling.

As has already been indicated, starch is susceptible to hydrolysis. On heating with aqueous mineral acids it is completely converted into glucose; by the action of certain enzymes, such as *diastase* (in malt) and *ptyalin* (in saliva), starch yields maltose (p. 280).

As intermediate products in the hydrolysis of starch are formed the **dextrins**, which can be more readily produced by heating starch alone—or, better, after the addition of a trace of nitric acid—to 110–120°. They are also produced as a by-product in the preparation of glucose by the hydrolysis of starch. The mixture of products thus obtained, usually called Dextrin, is a yellowish powder, soluble in cold water, which is employed for the preparation of dry adhesives and mucilage. The dextrins, being hydrolytic products of starch, differ chemically from it in that they possess reducing properties and react with phenylhydrazine.

Starches and dextrins show their alcoholic properties by their ability to form esters with inorganic and organic acids. A "hexanitrate" of starch $[C_{12}H_{14}O_{10}(NO_3)_6]_n$ is produced by the action of concentrated nitric acid. Such nitrostarches are

technically employed for the manufacture of paper sizes and adhesives. Starch is also capable of forming a series of acetates.

Glycogen is a carbohydrate, closely resembling starch, which occurs in many animal organisms, and is thought to be the reserve form of carbohydrates in animal life, like starch in plant life. It is found in considerable quantity in the livers of mammals, and in molluscs such as oysters. It is soluble in hot water, yielding an opalescent solution from which the glycogen does not separate on cooling. On hydrolysis with acids it yields glucose. It is readily distinguished from starch by the fact that it gives a reddish-brown coloration with a trace of iodine.

Inulin is a starch which is found in certain roots and tubers. Its chief feature of interest lies in the fact that on hydrolysis it yields exclusively fructose. With iodine it develops a pale yellow colour.

Cellulose is the generic term for a number of ill-defined substances of the empirical formula $(C_6H_{10}O_5)_n$. For the present purpose, however, we may consider the class as an individual.

Cellulose constitutes the chief solid material of the cell-walls of plants, and is therefore, in point of quantity, by far the most important of the carbohydrates.

Wood fibre contains a high proportion of cellulose; purified cotton is practically pure cellulose, and vegetable fibres such as hemp, jute, and linen, consist almost entirely of cellulose. Straw and grasses contain a considerable proportion of cellulose, and are employed in the manufacture of paper.

The properties of cellulose differ markedly from those of the sugars; it is absolutely insoluble in water, and is far more resistant to the action of dilute acids. For this reason it finds multitudinous application in the arts. Cotton and linen textures consist of cellulose fibres, frequently treated with earthy "loading" materials and varnishes or sizes; paper consists of cellulose pulp heavily loaded and sized. Filter paper, especially the ash-free qualities, is almost pure cellulose, without "load" or size.

Cellulose is, like starch, a complicated condensation product of glucose; it is stable towards hot dilute mineral acids, but it dissolves readily in cold concentrated sulphuric acid, thereby undergoing partial hydrolysis. If such a solution be diluted with water and then boiled, the solution ultimately contains nothing but glucose and sulphuric acid.

Full advantage has been taken of this fact by brewers; the occasional presence of arsenic in beer is due to the employment of

impure sulphuric acid prepared from arsenical pyrites. If cellulose be treated for a short time with sulphuric acid containing about 20 per cent. of water, it is converted into a tough mass; paper so treated is extremely strong and resistant, and is known as *parchment paper* or *vegetable parchment*. If treated with concentrated sulphuric acid at a temperature between 5° and 15° , cellulose is converted into a water-soluble starch-like substance, called *amyloid*, which develops a blue colour with iodine.

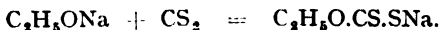
Less violent means of hydrolysis yield the so-called *hydro-cellulose*, which, whilst resembling cellulose in its insolubility in water and dilute acids, readily dissolves in aqueous alkalis and displays other points of difference. An *oxycellulose*, of similar properties, is produced by the action of certain oxidising agents, and closely resembles the *acid-cellulose* produced by the action of hot concentrated alkalis upon cellulose. A peculiar property of cellulose is that of forming loose compounds with alkalis: on treatment with cold 20 per cent. caustic soda, the so-called *soda-cellulose*, corresponding in composition with the formula:



is produced. This compound is regenerated into its components on treatment with excess of water.

Cellulose enters into solution in some rather unexpected liquids, such as a solution of cupric hydroxide in aqueous ammonia or an acid solution of zinc chloride. "Willesden paper" and "Willesden cloth" consist of paper or cellulose textile in which the surface has been treated with an ammoniacal solution of cupric hydroxide, the cellulose thus taken into solution being subsequently reprecipitated upon the fibres. By this means the material is rendered water-proof. "Mercerisation" is a similar process applied to cotton goods, in which the surface of the textile is, while under tension, softened by the action of strong aqueous sodium hydroxide. The material, after rolling and pressing, thus acquires a glossy appearance.

Certain chemical derivatives of cellulose, which have found wide application in the arts, are of interest in showing the alcoholic character of cellulose. It will be recalled (p. 183) that sodium ethoxide, on treatment with carbon disulphide, yields sodium ethyl xanthate or xanthogenate:



If soda-cellulose be treated with carbon disulphide, a water-soluble material is formed. This is sodium cellulose xanthate, and is manufactured under the name of "Viscose." It is decomposed on standing, or, more rapidly, on treatment with acids, yielding $\frac{1}{2}$ rocellulose.

Even more important are the nitrates of cellulose. If cellulose be treated with a mixture of concentrated sulphuric acid and nitric acid, it does not enter into solution, but the product, which closely resembles cellulose in appearance, possesses totally different properties. It is highly inflammable, and dissolves in certain liquids, such as acetone, in which cellulose itself is entirely insoluble. This product is *nitrocellulose*—a derivative of cellulose in which some or all of the hydroxyl groups are esterified with nitric acid (cf. nitroglycerine, p. 132). It is possible to prepare, by suitably altering the conditions of experiment, a series of nitric esters of cellulose in which varying proportions of the nitryl ($-\text{NO}_2$) radicle have entered the molecule. The highest possible nitrate is the so-called hexanitrate, of which the composition corresponds with the formula $[\text{C}_{12}\text{H}_{14}\text{O}_4(\text{O}.\text{NO}_2)_6]_n$.

From this we can conclude that for every twelve carbon atoms in the molecule of cellulose there are six hydroxyl groups, leading to the provisional formula $[\text{C}_{12}\text{H}_{14}\text{O}_4(\text{OH})_6]_n$ for cellulose. Lower esters of cellulose have been shown to be capable of existence, although they have not been isolated in a pure condition. The higher nitrates are employed as explosives, occasionally with the admixture of nitroglycerine and other substances; the lower nitrates are employed for the manufacture of celluloid articles. Celluloid consists of a mixture containing chiefly tetra- and pentanitrates, together with camphor, which renders the product less brittle.

Collodion is the name given to a solution of nitrocellulose in a mixture of alcohol and ether. Fine threads of this material can be drawn and spun; when woven, they closely resemble silk. Owing, however, to the inflammable nature of such a texture, the product cannot be employed in this condition for wear, but must first be *denitrated*. This is effected by treatment with substances such as ammonium sulphide, which reduce and thus remove the nitryl groups (cf. p. 194), leaving behind a texture of hydrocellulose, which has every appearance of natural silk.

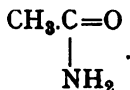
Esters of organic acids with cellulose are also known; such are cellulose formates, acetates, butyrates, and even palmitates. The most important of these are the acetates, of which a series corresponding to the nitrates, up to hexa-acetate $[\text{C}_{12}\text{H}_{14}\text{O}_4(\text{O}.\text{CO}.\text{CH}_3)_6]_n$, exist.

Cellulose forms an analogous series of alkyl ethers, typical of which is the hexaethyl ether $[\text{C}_{12}\text{H}_{14}\text{O}_4(\text{OC}_2\text{H}_5)_6]_n$.

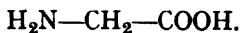
CHAPTER XXII

AMINO ACIDS

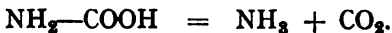
THE amino acids, also called *amido acids*, must not be confounded with the acid amides. It will be recalled that acid amides are derivatives of carboxylic acids in which the hydroxyl group of the carboxyl (—COOH) radicle is replaced by an amino (—NH_2) group. A typical acid amide is acetamide, the amide of acetic acid :



Amino acids, on the other hand, are carboxylic acids in which a *hydrogen* atom directly attached to carbon is replaced by an amino group. They are thus in chemical structure true amines (p. 198), like methylamine $\text{H}_3\text{C—NH}_2$. The simplest member of the series is aminoacetic acid :



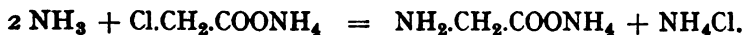
The corresponding derivative of formic acid, carbamic acid (p. 181) $\text{H}_2\text{N.CO.OH}$, cannot be regarded as a true amino acid, but rather as a semi-amide of carbonic acid, HO.CO.OH . As a matter of fact, free aminoformic acid is incapable of independent existence, and breaks down at once into carbon dioxide and ammonia :



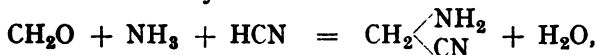
Amino acids may thus be regarded either as amines in which one or more carboxyl groups replace hydrogen atoms attached to carbon, or as carboxylic acids in which hydrogen

atoms not attached to the carboxyl group are replaced by amino groups. The chemical character of the molecule as a whole is, of course, influenced by the presence of both basic and acidic radicles.

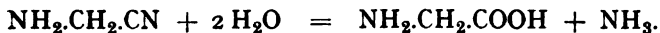
Aminoacetic acid $\text{NH}_2\text{CH}_2\text{COOH}$, also called *glycine* or *glycocoll*, is prepared by the action of ammonia upon chloroacetic acid :



Another method of formation of amino acids is the simultaneous action of ammonia and hydrogen cyanide upon aldehydes, with subsequent hydrolysis of the product. Formaldehyde reacts thus with ammonium cyanide :



and this amino-nitrile yields glycine on hydrolysis :

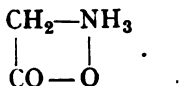


This is a general reaction, applicable to all aldehydes. Glycine is also produced by the hydrolysis of gelatin by boiling with aqueous mineral acids.

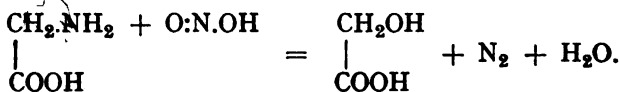
As might be expected, glycine behaves both as an acid and as a base : it forms salts with metals, such as sodium aminoacetate, $\text{NH}_2\text{CH}_2\text{COONa}$; and salts with acids, such as glycine hydrochloride, $\text{HCl}\cdot\text{NH}_2\text{CH}_2\text{COOH}$.

Glycine is a colourless crystalline substance which melts with decomposition at 237° . It is extremely soluble in water, yielding a neutral solution possessing a sweetish taste ; it is insoluble in absolute alcohol and in ether.

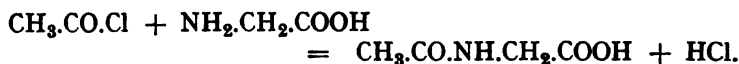
The fact that glycine shows neither acid nor alkaline reaction towards litmus is attributed to the formation of an internal salt between the basic amino radicle and the acidic carboxyl group. Such a view involves a cyclic formulation of glycine, thereby representing it as an ammonium salt :



Glycine hydrochloride, on the other hand, shows well-defined acid properties. In this case the basic qualities of the amino group are neutralised by the hydrochloric acid, leaving the carboxyl group free to exercise its normal functions. Similarly, if the acid character of the carboxyl group be removed, as by esterification, the resulting compound, in this case, ethyl aminoacetate $\text{NH}_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$, possesses distinctly basic qualities. Glycine behaves towards nitrous acid in the manner common to primary amines (p. 201), yielding nitrogen and glycollic acid :

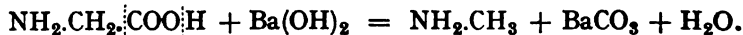


It may also be acylated like any other primary amine ; with acetyl chloride it yields *acetylaminooacetic acid* :



Just as in acetamide the basic character of the amino group is reduced by the acetyl ($\text{CH}_3\cdot\text{CO}-$) radicle, so is it also in this case, with the result that acetylaminooacetic acid possesses a markedly acid character. An analogous compound, *benzoylaminoacetic acid* $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, in which an amino hydrogen atom is replaced by the *benzoyl* radicle ($\text{C}_6\text{H}_5\cdot\text{CO}-$; p. 391), is of physiological importance in that it is the end-product of nitrogenous metabolism of many herbivores. It is generally known as *hippuric acid* (p. 394).

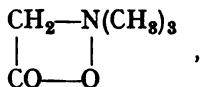
On heating with barium hydroxide, glycine breaks down into methylamine and carbon dioxide :



Characteristic of glycine and of many other amino acids is their faculty of forming well-crystalline copper salts, which have an intense blue colour. This property is utilised in the preparation of glycine from chloroacetic acid : after the completion of the reaction between ammonia and chloroacetic acid, the excess of ammonia is removed in a current of steam, and the glycine converted into its copper salt $(\text{NH}_2\cdot\text{CH}_2\cdot\text{COO})_2\text{Cu} + \text{H}_2\text{O}$ by treatment with copper carbonate. This is then separated in a pure crystalline condition and decomposed in aqueous solution by means of hydrogen

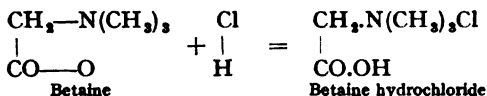
sulphide. The aqueous solution, after removal of the copper sulphide and the excess of hydrogen sulphide, contains pure glycine.

On complete methylation, glycine is converted into **betaine** or *trimethylglycine*, a substance which is present in the beet-juice residues after the extraction of the sugar (p. 282). Betaine has the formula :



and is thus a quarternary ammonium compound.

It crystallises with one molecule of water, which it loses at 100° . It is a neutral substance, but forms with acids stable salts, which possess the definite acid properties of carboxylic acids :

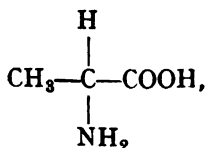


Betaine hydrochloride is also produced by the interaction of chloroacetic acid with trimethylamine :



On dry distillation, betaine breaks down into carbon dioxide and trimethylamine.

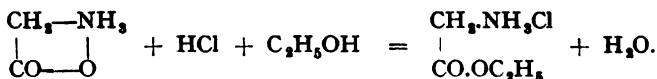
Homologues of glycine are known in considerable number, many of them appearing as products of the hydrolysis of various proteins (see below), just as gelatin yields glycine. Such are **alanine** or *α -aminopropionic acid* $\text{CH}_3\text{.CH(NH}_2\text{).COOH}$; **valine** or *amino-iso-valerianic acid* $(\text{CH}_3)_2\text{CH.CH(NH}_2\text{).COOH}$; and **leucine**, or *α -amino-iso-capric acid* $(\text{CH}_3)_2\text{CH.CH}_2\text{.CH(NH}_2\text{).COOH}$. It will be observed that in all of these, the amino group is attached to the α -carbon atom—the same carbon atom to which the carboxyl group is attached. With the exception of glycine, these amino acids all contain an asymmetric carbon atom—as for instance in alanine :



and, in conformity with the theory, can be obtained in optically active stereoisomers. All the amino acids, except glycine, obtained by the hydrolysis of proteins have been found to be optically active.

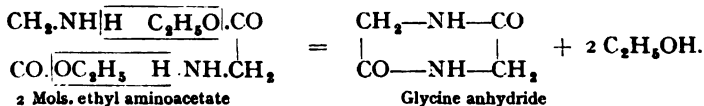
The properties of these homologues resemble those of glycine with such close analogy that no detailed description is here necessary.

If an amino acid be treated with absolute alcohol, and a stream of dry hydrogen chloride passed through the mixture, the hydrochloride of the corresponding ethyl ester is produced :

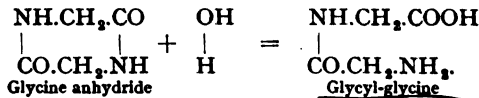


The free ester, in this case ethyl aminoacetate, can be liberated from the hydrochloride by the action of alkalis.

When such an ester is heated, or allowed to stand in aqueous solution, a condensation takes place—similar to the formation of amides by the action of ammonia on esters (p. 173)—whereby two molecules condense together with elimination of alcohol to form a cyclic compound :



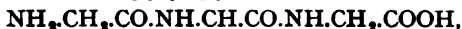
Such a compound, which is a close analogue of a lactide (p. 244), is termed an *amino acid anhydride*. Its chief interest lies in the fact that on partial hydrolysis the ring is broken with formation of a *dipeptide* :



This dipeptide glycyl-glycine is a compound analogous to acetyl glycine $\text{CH}_3\text{CO.NH.CH}_2\text{COOH}$, differing only in that the acetyl group is here replaced by an aminoacetyl group. It is of course equally possible to prepare similar compounds from other amino acids, for example, *alanyl-alanine* :



Emil Fischer, in his elucidation of the constitution of the proteins, has, by the use of different synthetic methods, extended this class of compounds by preparing long chains of amino acid radicles connected in this way. Such compounds he has termed *polypeptides*. He has not only been able to prepare chains of the same radicle, such as *diglycyl-glycine*



but has produced chains built up of the radicles of different amino acids, for example, *leucyl-triglycyl-glycine*



He was led to the synthesis of these compounds by the occurrence of such bodies in the products of partial hydrolysis of proteins, and was ultimately able, by employing optically pure amino acids (that is, amino acids consisting entirely of one of the optical antipodes), to prepare substances which display many of the characteristics of natural proteins. One of these bodies is a condensation-product of no less than eighteen amino acid radicles.

Proteins, also termed *proteids* or *albumins*, which have above been mentioned as yielding amino acids on hydrolysis, constitute a large and complex family of nitrogenous compounds which occur in animal and vegetable organisms. As has already been indicated, they are regarded as elaborate condensation-products of different amino acids, strung together as are the components of the polypeptides of Fischer.

Animal and vegetable tissues consist principally of water, carbohydrates, fats and proteins, from which it will be seen that the bulk of the combined nitrogen of living organisms is in the form of protein. Physiological chemists claim to have isolated a number of different proteins, but it is questionable whether these substances are pure chemical individuals, since the majority are amorphous solids which yield colloidal solutions, to which no tests of chemical homogeneity can be applied. A few proteins, however, can be obtained in a crystalline form; such are the *albumin* from white of egg, the *hemoglobins* from the blood, and certain proteins occurring in seeds and nuts; and in the case of such crystalline bodies it is possible, though by no means proved, that we are dealing with pure chemical individuals.

The molecular weights of the proteins are extremely high; such determinations as have been made by physical methods, though by no means to be regarded as strictly accurate, point to molecular weights of several thousands. Another indication of the high molecular weight of proteins is afforded by their chemical composition. Almost all these substances contain a small proportion of combined sulphur, and since one molecule of the protein

contains at least one atom of sulphur, an estimate of the minimum molecular weight can be made. For example, analysis of a substance called *globulin*, which occurs in blood serum, is stated to lead to an empirical formula $C_{821}H_{814}O_{169}N_{178}S$, corresponding with a molecular weight of not less than 13,452.

Hæmoglobins afford another instance. In the hæmoglobin which forms the red colouring matter of dog's blood—as in the other hæmoglobins from other sources—there is a small proportion of iron, existing in a combined form. From analysis of this substance, the simplest formula by which the composition can be expressed is $C_{758}H_{1203}O_{218}N_{198}S_2Fe$, whence the minimum molecular weight must be 16,669. The physical determinations, such as they are, of the molecular weights of the proteins, lead to figures of the same order of magnitude.

As above stated, proteins on hydrolysis by boiling with aqueous mineral acids are almost quantitatively broken down into amino acids. A similar effect can be brought about by the proteolytic enzymes, *e.g.* pepsin, occurring in animal organisms, but in this latter case intermediate products—termed *albumoses* and *peptones*—can be isolated, which consist of mixtures of substances which not only resemble in character, but in some cases are identical with, the polypeptides of Fischer. These can, on further hydrolysis, be broken down into simple amino acids.

The mixtures of amino acids produced by the hydrolysis of different proteins vary widely in composition. Thus gelatine yields a large proportion of glycine, whilst others yield only traces. As a rule, about ten to twenty different amino acids can be isolated from each individual protein, the proportions of these varying markedly with the different proteins. Besides glycine and its homologues mentioned on p. 291, other important aliphatic amino acids produced from proteins are :

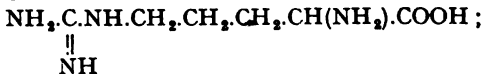
Aspartic acid, or aminosuccinic acid, $COOH.CH_2.CH(NH_2).COOH$;
Glutamic acid, or α -aminoglutaric acid,



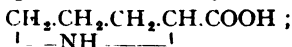
Lysine, or α - ϵ -diamino-*n*-capric acid,



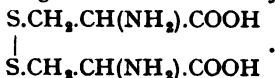
Arginine, a guanidine derivative of lysine,



Proline, a cyclic compound related to lysine,



and a sulphur-containing amino acid called *cystine*



In addition to these, there are also some "aromatic" (see p. 300) amino acids, of which the most important are *phenylalanine*, $\text{C}_6\text{H}_5\text{.CH}_2\text{.CH(NH}_2\text{).COOH}$, and *tyrosine*,



as well as some of more complicated structure, for instance, *histidine* and *tryptophane*, the presentation of the formulæ for which would only lead to confusion in this place. All these acids, when obtained from proteins, are pure optically active compounds.

The following qualitative tests are characteristic of proteins in general :

(1) Biuret reaction : on adding to a solution of the protein in 10 per cent. sodium hydroxide a few drops of copper sulphate solution, a blue-violet coloration is produced, this being intensified on boiling.

(2) Millon's reaction : on adding a solution of mercurous nitrate in dilute nitric acid to an aqueous solution of a protein, a whitish precipitate is produced, which turns red on boiling.

(3) Adamkiewicz's reaction : to a solution of a protein in water, a small quantity of glyoxylic acid (p. 258) is added. On pouring concentrated sulphuric acid into the mixture so that it forms a distinct lower layer, a violet ring is formed at the junction of the liquids.

Finally, many proteins, on treatment with concentrated nitric acid, assume an intense yellow colour ; and all proteins, on strongly heating, evolve the characteristic odour emitted by burning animal matter, such as hair or feathers.

CHAPTER XXIII

URIC ACID AND PURINES

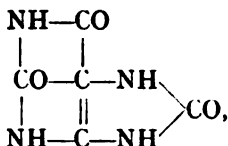
Uric acid is a compound of great physiological importance, and on this account must find mention here ; from a purely chemical point of view a thorough study of its theory is a matter of rather too great difficulty at this stage, for it bears but little resemblance to the types of compound hitherto discussed. For this reason it must here be viewed more from a practical than from a theoretical standpoint.

Uric acid occurs as a normal constituent of mammal urine, which contains quantities varying from 0.1 to 0.5 gram per litre under healthy conditions. It appears, however, to form the end-product of nitrogenous metabolism in birds and reptiles, being the principal constituent of the excreta of these animals. In the fæces of serpents the bulk of the solids consists of ammonium urate, whilst guano—the sun-dried excrement of sea-fowl—is rich in uric acid, and forms its principal source of supply. It is of importance in human medicine as forming a considerable fraction of the composition of urinary calculi ; in all cases of gout the presence of deposits of crystals of sodium urate in the joints of arms, legs, shoulders, etc., is observed, indicating a pathological over-production of uric acid by the system.

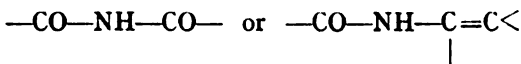
Uric acid itself is a white crystalline substance of the composition $C_5H_4O_3N_4$, which is almost insoluble in water. The sodium salt $C_5H_3O_3N_4.Na$ is sparingly soluble ; the neutral lithium salt $C_5H_2O_3N_4Li_2$ dissolves much more readily, for which reason lithia is administered in cases of gout. In normal human urine, uric acid usually exists in the form of the ammonium salt $C_5H_3O_3N_4.NH_4$; on acidifying a sample of urine with

hydrochloric acid, the uric acid slowly separates as a crystalline deposit. It can be quantitatively estimated by titrating with standard acid permanganate, by which it, in a warm solution, is rapidly oxidised.

The chemical behaviour of uric acid leads to the following constitution :

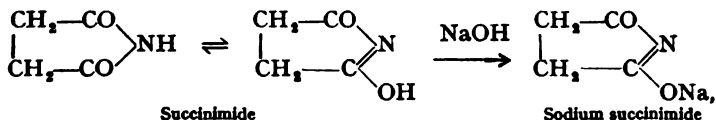


and this view has been supported by several syntheses. The natural question—how a compound of such a structure, containing no carboxyl groups, can function as an acid—can be answered by the statement that in compounds containing the structures

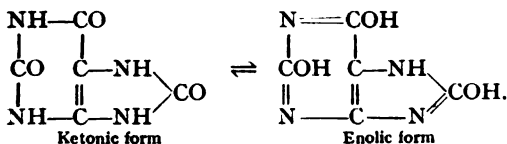


the hydrogen atom can readily be replaced by a metal. Examples of such compounds are cyanuric acid (p. 224) and succinimide (p. 191), which form derivatives of sodium or potassium.

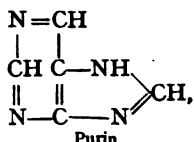
It is possible to regard such metallic compounds as derivatives of *enolic* (p. 261) forms ; we could thus formulate succinimide and its sodium derivative in the following manner :



succinimide thus appearing as a tautomeric compound. In the same way we can formulate uric acid tautomerically :

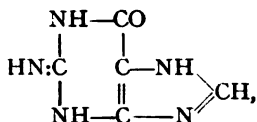


The enolic form of uric acid may be considered as a trihydroxylic derivative of a substance of the formula :



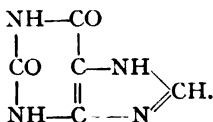
which Emil Fischer, the chemist whose work decided the constitution of uric acid and its relatives, has termed **Purin**.

A member of the purin family, which occurs together with uric acid in guano, is **guanin**. This possesses the constitutional formula :

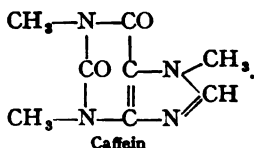
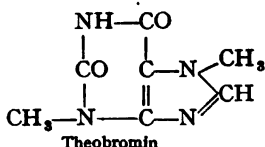


from which its relation, on the one hand to purin, on the other hand to guanidine (p. 182), can readily be perceived. It differs from uric acid in showing distinctly basic properties.

Xanthin, a substance closely related to uric acid, which occurs in meat and in certain vegetable products, has the formula :



Its methyl derivatives are of importance as constituting the physiologically active principles of three of our chief beverages. **Theobromin**, or *dimethylxanthin*, is present in cocoa ; **cafein**, or *trimethylxanthin*, occurs in tea and in coffee :



Cafein, which is now largely employed in medicine, is manufactured on a considerable scale from uric acid, obtained from guano.

A qualitative test which is given by all the members of the

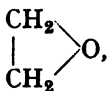
purine group is the *murexide* test : a small quantity of the substance is treated with a few drops of chlorine water or nitric acid, and the mixture evaporated to dryness on the water-bath. On adding to the red-coloured residue a few drops of ammonia or caustic soda solution, an intense purple coloration is produced.

CHAPTER XXIV

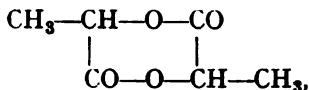
AROMATIC COMPOUNDS

BENZENE

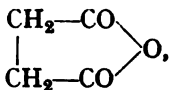
Up to the present we have concerned ourselves principally with open-chain substances, that is to say, with derivatives of hydrocarbons containing normal or branched chains, such as the fatty acids. It is true that some compounds of *cyclic* structure have been mentioned, such for instance as ethylene oxide



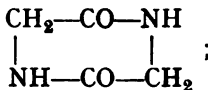
lactide



succinic anhydride



and glycine anhydride



but in these substances atoms of oxygen or nitrogen form members of the ring. The division of organic chemistry, in short, with which we have hitherto dealt has been the *aliphatic* division—the chemistry of the derivatives of open-chain saturated and unsaturated compounds. The term “aliphatic,” derived from the Greek word *ἄλειφος* signifying “unguent,”

was applied in the early days of organic chemistry to the class of substances which then appeared to be more or less intimately related to the fats.

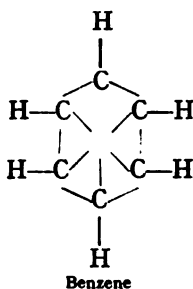
At the time when this term was applied, chemists were acquainted with a few bodies, all of which chanced to possess aromatic odours, between which and the fatty compounds no genetic relations could be traced. These compounds consisted chiefly of the essential oils of fruits and plants, such as oil of bitter almonds, as well as certain natural resins, such as gum benzoin. Our increased knowledge of chemistry has afforded us an insight into the nature of most of these aromatic products, and we now recognise that in principle they do not fundamentally differ from other organic compounds; it has nevertheless been found convenient to retain the epithet, while associating its sense with a totally different idea. Just as aliphatic compounds may be regarded as substances derived from methane, so have all these natural aromatic compounds been shown to be similarly related to a hydrocarbon called **benzene**; and, following out this idea, the term "aromatic" is now applied to all derivatives of this substance, whether they be endowed with aromatic qualities (in the original sense of the word) or not. It will be recalled that a similar transference of ideas has taken place with regard to the sense of the word "organic."

Characteristic of aromatic compounds is the fact that all contain at least six atoms of carbon in the molecule. Benzene itself has the composition and molecular weight corresponding with the empirical formula C_6H_6 ; so that derivatives of this substance cannot, unless they be produced by reactions so profound as to be virtually destructive, contain less than the original six atoms of carbon in the molecule.

Now, according to the rules governing aliphatic hydrocarbons, benzene should be a highly unsaturated compound, for the formula corresponds with C_nH_{2n-6} . It will be recalled that the saturated (paraffin) hydrocarbons are composed of carbon and hydrogen in the proportions given by C_nH_{2n+2} . Nevertheless, benzene is extremely stable towards oxidising agents of all sorts—a behaviour incompatible with the ideas which we have

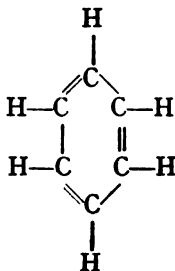
hitherto held on the properties of unsaturated compounds. It is therefore obvious that in benzene we have to deal with a totally new class of phenomena.

With regard to the structural conditions obtaining in benzene, it must at once be confessed that our knowledge is far from complete. What is certain, however, is that the molecule consists of a ring of six carbon atoms, to each of which one hydrogen atom is attached. The distribution of the fourth valency of each carbon atom is left out of account :

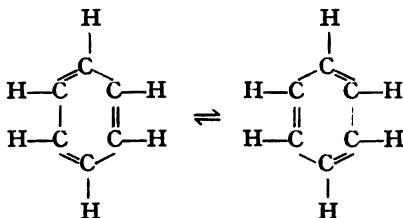


A few of the numerous proofs of the correctness of this view will appear in the course of the text.

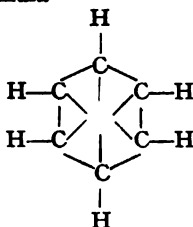
It will be observed that the above formulation of benzene is, as it stands, in flat contradiction to the assumption of the constant quadrivalency of the carbon atom, since here the carbon atoms are represented as tervalent. The original proposal of Kekulé, who pointed out the necessity of formulating benzene as a six-membered ring, was that the fourth valency should be indicated by an alternating disposal of double bonds :



In order, however, to meet certain objections, he was forced to add the supplementary postulate that these double bonds were continually shifting their positions, resulting in a condition of equilibrium expressed by :



Another convention, proposed by Baeyer and Armstrong, is the so-called "centric" formula



in which the fourth valencies of the carbon atoms are represented as all saturating themselves together in the centre of the cyclic system.

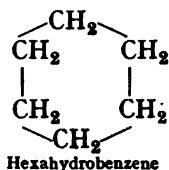
These methods of formulation are for our present purposes little more than meaningless; we are, by their aid, in no way advanced in our knowledge of the inward nature of benzene. A stereochemical formula, proposed by Collie, in which it is shown how the atoms may possibly be related in space, and how they may vibrate with reference to each other, gives the most satisfactory correlation of the various phenomena hitherto observed, but is of too complicated a nature to be here set forth.

What chiefly concerns us is to make use of a convenient symbol by which the properties of the substance in question may—by suitably reading certain understood facts into the formula—be simply and adequately described. This is met by the use of the chemical shorthand sign :

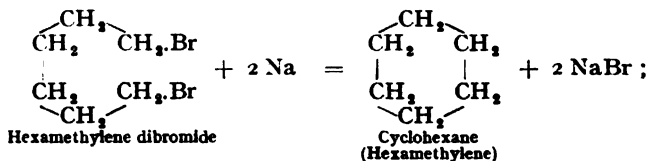


a simple hexagon. By its use we are able to convey the necessary ideas of chemical behaviour, and leave open the unprofitable questions of controversy.

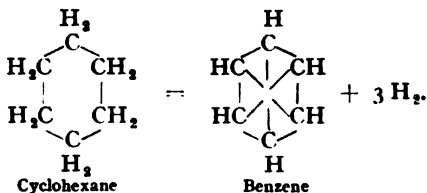
When benzene is treated with powerful hydrogenating agents, as, for instance, with hydrogen under the catalytic influence of certain finely-divided metals, six atoms of hydrogen are taken up, yielding a hydrocarbon C_6H_{12} of the formula :



That this formulation is correct is shown by the identity of hexahydrobenzene with cyclohexane (also called hexamethylene), produced by the action of sodium upon hexamethylene dibromide (α - β -dibromo-*n*-hexane) :



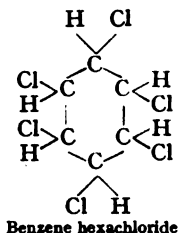
and the fact that cyclohexane, on treatment with spongy platinum at 300° , is quantitatively converted into benzene and hydrogen :



This proves that the structure of benzene consists of six carbon atoms arranged in a six-membered ring. It will be shown later that the hydrogen atoms in benzene can be substituted by other atoms or groups : thus on treatment with

chlorine, chloro-benzene C_6H_5Cl is produced. This is analogous to the relation of methane and chloromethane. Now only one chlorobenzene C_6H_5Cl is known, and exhaustive experiments have shown that, whatever the method of its formation, the same chlorobenzene is always produced. From this fact we conclude that all the hydrogen atoms in benzene are equivalent—replacement of any one of the six leads always to the same mono-substituted derivative. The only possible method then, by which we can express this fact, is to formulate benzene as having one hydrogen atom attached to each carbon atom.

Benzene can, under certain circumstances, be made to form an addition-product $C_6H_6Cl_6$ with chlorine. This addition, however, does not take place with even approximately the same readiness that aliphatic unsaturated compounds display in uniting with chlorine. The product can take up no more chlorine additively, and must be regarded as fully saturated. It is a hexachloro-derivative of cyclohexane :



An aliphatic unsaturated hydrocarbon isomeric with benzene would be expected to form an octochloro- addition-product $C_6H_6Cl_8$. Such a hydrocarbon is the diacetylenic compound *dipropargyl* $CH_3C \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_3$, which forms the octochloride

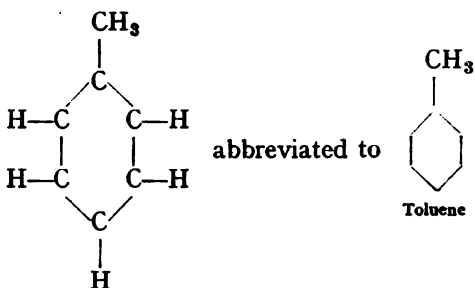


on treatment with chlorine.

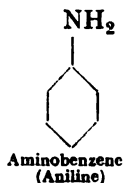
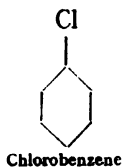
SUBSTITUTION AND ISOMERISM

The hydrogen atoms in benzene, like those of methane, can be replaced by other atoms or groups. Analogous to ethane (methyl-methane) is toluene (*methyl-benzene*) :

x



Similarly, the hydrogen atoms may also be replaced by such radicles as chlorine atoms and amino groups, giving :



analogous to methyl chloride and methylamine. It will be observed that, in the system of formulation based upon the simple hexagon, where the corners of the hexagon are left without chemical symbols, a hydrogen atom is understood to be attached to the corresponding carbon atom of the benzene nucleus.

This analogy with methane does not extend beyond the monosubstitution-products. The chlorine-substituted derivatives of benzene may be discussed in order to illustrate the condition. In the first chapter it was pointed out that only one monochloromethane, one dichloromethane, one trichloromethane, and one tetrachloromethane, are known. In the chloro derivatives of benzene, only one monochlorobenzene is known :



That is to say, the carbon atoms 1, 2, 3, 4, 5, and 6 in benzene, and the hydrogen atoms attached thereto, are absolutely equivalent.

In the dichlorobenzenes a new type of isomerism is introduced. From purely geometrical considerations, we might here expect three different products, expressed by the formulæ :



I



II

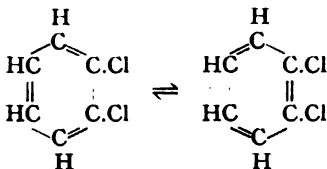


Cl

III

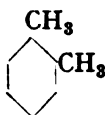
This is in accord with the observed facts, affording a further justification for the employment of the plane hexagonal formula for benzene. Three different dichlorobenzenes are known, possessing totally distinct properties, and from these properties it has been found possible to associate each of these three dichlorobenzenes with one of the three formulæ given above. The first (I) is known as *ortho* dichlorobenzene, the second (II) is called *meta* dichlorobenzene, and the third (III) is termed *para* dichlorobenzene.

The original benzene formula of Kekulé called for the existence of two series of *ortho* disubstituted derivatives of benzene, according as to whether a single bond or a double bond united the two carbon atoms to which the substituents were attached. But only one such series exists—only one dichlorobenzene, for instance, is known. In order to make the formula meet this fact, the hypothesis of continual alternation of double linkages had to be introduced :

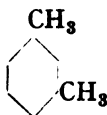


Similar relations are found in all the other classes of

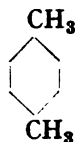
disubstituted derivatives of benzene. Thus, for example, in the dimethylbenzenes, or **xylene**s, we have :



Ortho xylene

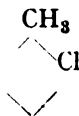


Meta xylene

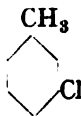


Para xylene

in the chloro-methylbenzenes, or *chlorotoluenes*, three isomers are known :



Ortho chlorotoluene



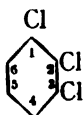
Meta chlorotoluene



Para chlorotoluene

This list of examples might be extended almost indefinitely. It is customary to abbreviate the prefixes *ortho*, *meta*, and *para*, to *o*-, *m*-, and *p*-, respectively.

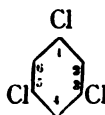
When three of the hydrogen atoms of benzene are substituted, as in the trichlorobenzenes, we have the following possibilities :



I



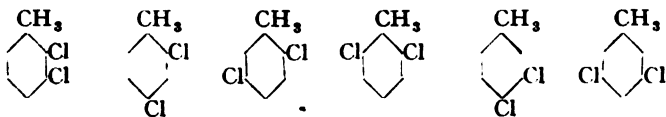
II



III

Three, and only three, trichlorobenzenes are known, and our theory allows for the existence of only three. It is usual to name such compounds by numbering the carbon atoms in a ring : (I) is termed *1.2.3-trichlorobenzene* ; (II) is *1.2.4-* (or *1.3.4-*) *trichlorobenzene* ; (III) is *1.3.5-trichlorobenzene*.

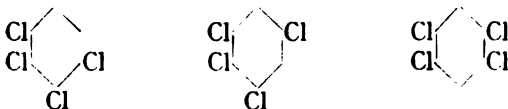
When the substituent atoms or groups are not the same, the possibility of isomerism becomes greater. The following formulae will illustrate this :



Isomeric dichlorotoluenes

Compounds corresponding with all these formulæ are known. When the three substituents are all different from one another, as for instance in the chlorobromotoluenes, no less than ten isomers are to be found.

In tetrasubstituted derivatives of benzene we shall consider only those in which the constituent groups are the same ; when they are different, the possibility of isomerism becomes too great to be here expounded. To take the case of the tetrachlorobenzenes, it is obvious that only three isomers can exist, namely compounds in which the unsubstituted hydrogen atoms are respectively in the *ortho*, *meta*, and *para* positions relatively to each other :



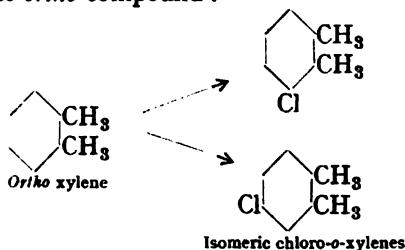
Isomeric tetrachlorobenzenes

In the same way, only one pentachlorobenzene and one hexachlorobenzene are capable of existence in accordance with the theory, and only one of each is known :

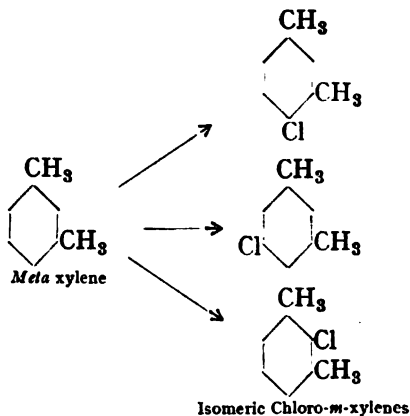


It may be well here to inquire into the evidence upon the strength of which we have been able to associate the different substances with their appropriate formulæ. The most conclusive and fundamental of the methods is the "absolute method of orientation" of disubstituted derivatives, devised by Koerner. This method may be made clear by considering as examples the three isomeric xylenes (dimethylbenzenes).

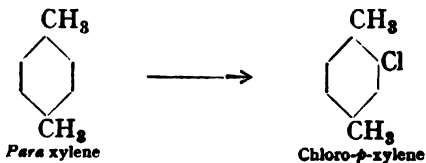
If we cause a third substituent, such as chlorine, to enter the nucleus in each case, each isomer is capable of yielding a different number of products. It has been found that from one of the xylenes, two, and only two, monochloro derivatives can be obtained ; from a second, three can be produced ; while the third is capable of yielding only one. The first must therefore be the *ortho* compound :



The second must be the *meta* compound :



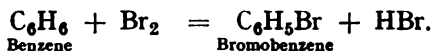
The third must be the *para* compound :



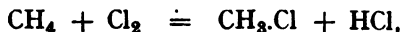
This system of orientation can be continued, by similar processes of observation and reasoning, to the derivatives of benzene containing more than two substituents.

OTHER SUBSTITUTION-PRODUCTS OF BENZENE

Up to the present our discussion has been confined principally to the methyl- and chloro- substitution-products of benzene. It may here be well to enumerate a few of the many other important substituents which can replace the hydrogen atoms in benzene. In the halogen series, we have fluorine, chlorine, bromine, and iodine ; all of these can exist in combination with the benzene nucleus, in the form of such compounds as fluorobenzene C_6H_5F , chlorobenzene C_6H_5Cl , bromobenzene C_6H_5Br , and iodobenzene C_6H_5I . Chlorobenzene and bromobenzene, and their homologues, such as the chlorotoluenes, $CH_3.C_6H_4.Cl$, as well as compounds containing more than one halogen atom, such as the dibromobenzenes $C_6H_4Br_2$, can be prepared by direct action of the halogens upon benzene or its homologues ; for example :



This process of *chlorination* or *bromination* is similar in character to the action of chlorine on methane :



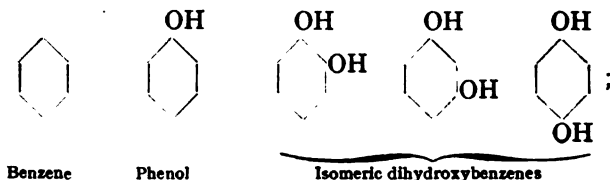
but is more easily controlled.

The hydrogen atoms of benzene may likewise be replaced by hydroxyl groups. The prototype of such substances is hydroxybenzene, generally called *phenol* :



Further oxidation to corresponding aldehydes and acids is not possible, since in benzene there is only one hydrogen atom attached to each carbon atom, which is available for substitution

by hydroxyl groups. Progressive replacement of hydrogen atoms in benzene by hydroxyl groups leads thus not to aldehydes and acids, but to di- tri-, etc., hydroxylic compounds. This is indicated by the series of formulæ :



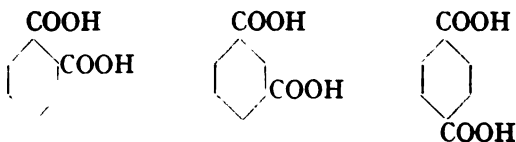
and so on.

A strict analogy is afforded by comparing ethane and toluene, and their products of progressive oxidation :

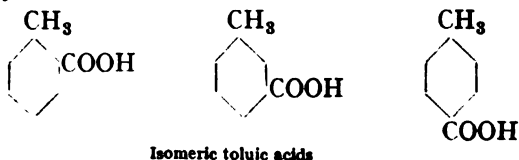
Ethane	$\text{CH}_3.\text{CH}_3$	Toluene	$\text{C}_6\text{H}_5.\text{CH}_3$
Ethyl alcohol	$\text{CH}_3.\text{CH}_2\text{OH}$	Benzyl alcohol	$\text{C}_6\text{H}_5.\text{CH}_2\text{OH}$
Acetaldehyde	$\text{CH}_3.\text{CHO}$	Benzaldehyde	$\text{C}_6\text{H}_5.\text{CHO}$
Acetic acid	$\text{CH}_3.\text{COOH}$	Benzoic acid	$\text{C}_6\text{H}_5.\text{COOH}$

We see here a few of the groups by which the hydrogen atoms of benzene may be substituted ; when it is remembered that all six of the hydrogen atoms may be replaced by such groups, an idea can be formed of the enormous number of simple derivatives of benzene.

As examples of these we need only mention the three dicarboxylic acids :

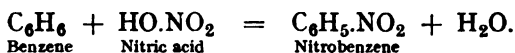


and the three isomeric acids containing one methyl group and one carboxyl radicle :

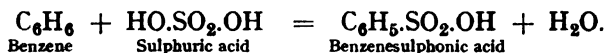


A practically unlimited number of formulæ of similar or more complicated derivatives of benzene may be worked out on paper—and it is not too much to say that the majority of formulæ which can thus be evolved correspond to known substances.

In some important particulars, benzene and its derivatives differ markedly from the aliphatic compounds which we have hitherto considered. Chief of these is the readiness with which certain inorganic hydroxylic compounds, such as nitric acid and sulphuric acid, can be caused to react. On treating benzene with concentrated nitric acid, the elements of water are removed, and *nitrobenzene* (cf. nitromethane, p. 207) results :



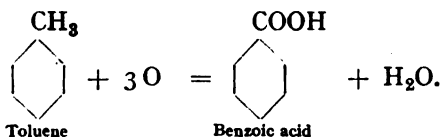
Similarly, on heating benzene with concentrated sulphuric acid, *benzenesulphonic acid* is formed :



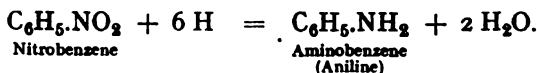
Reactions similar to these can be brought about with aliphatic hydrocarbons only with the greatest difficulty.

Another characteristic property of benzene, in which it differs markedly from the unsaturated aliphatic hydrocarbons, and resembles more closely the paraffins, is its resistance to oxidising agents. Benzene is not attacked by such oxidising agents as permanganate or chromic acid under conditions in which unsaturated aliphatic hydrocarbons would at once be oxidised.

On the other hand, aromatic hydrocarbons containing alkyl groups attached to the nucleus, such for instance as toluene, can readily be oxidised, yielding carboxylic acids. In this way toluene yields *benzoic acid* :



Nitrobenzene and other aromatic nitro compounds are converted on reduction into *primary amines*, which form an important class of aromatic compounds :

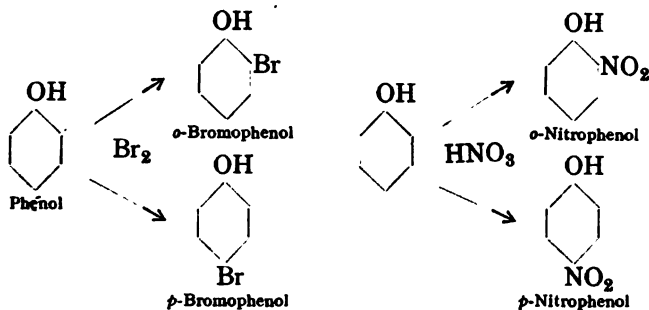


In conclusion, it may safely be stated that all atoms and groups which can replace hydrogen atoms in methane are also capable of replacing hydrogen atoms in benzene. In view of this fact it will not be necessary to draw attention at present to any further classes of substitution-products of benzene.

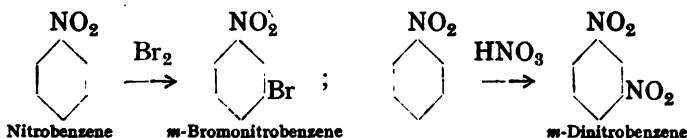
RULES OF SUBSTITUTION

When benzene is subjected to the action of substituting agents—such as chlorine, bromine, nitric acid, or sulphuric acid, the first product is always a monosubstituted derivative; and it has been pointed out that isomerism in such monosubstitution products has never been observed and is not provided for by the theory. On further substitution, introducing either the same or a different substituent, there exists the possibility of obtaining three distinct isomeric disubstitution-products, namely those in which the substituent groups are situated relatively in the *ortho*, *meta*, or *para* positions.

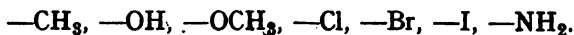
Experience has shown that in such a case mixtures of comparable quantities of all three isomers are never produced; the resultant product consists either of a mixture composed almost exclusively of the *ortho* and *para* isomers, or else of the *meta* isomer in preponderating quantity. Which of the two classes of action takes place has been shown to depend entirely upon the nature of the first substituent, and is independent of the nature of the entering radicle. To take an example—phenol (hydroxybenzene), on treatment with halogen, nitric acid, or sulphuric acid, yields mixtures of the isomeric *ortho* and *para* substituted phenols :



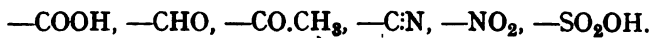
The *meta* derivatives are not formed. On the other hand, nitrobenzene, on treatment in a similar way, yields exclusively *meta* derivatives:



We may thus divide substituent radicles into two classes, the first of which leads to the formation of *ortho* and *para* derivatives, the second yielding *meta* derivatives. The more important members of the first class are :



The chief members of the second group are :



This generalisation is known as the "Crum-Brown Rule."

It is essential for the student to associate the various radicles with their respective classes, but there is no need for him to burden his memory with the above lists, since an empirical rule has been discovered, by which a radicle may at once be assigned to its appropriate class. This rule runs as follows : the radicle in question must be imagined as being attached to a hydrogen atom—H.R ; if the resulting compound on direct

oxidation can be made to yield the corresponding hydroxylic compound HO.R , then the radicle R belongs to the second class; if this reaction is known not to take place, then the radicle belongs to the first class. A few examples will make this clear:

$\text{R} = \text{CH}_3$. H.CH_3 = methane, which does not yield methyl alcohol HO.CH_3 on direct oxidation; whence $-\text{CH}_3$ belongs to the first class.

$\text{R} = \text{COOH}$. H.COOH = formic acid, which is readily oxidised to carbonic acid HO.COOH ; whence $-\text{COOH}$ belongs to the second class.

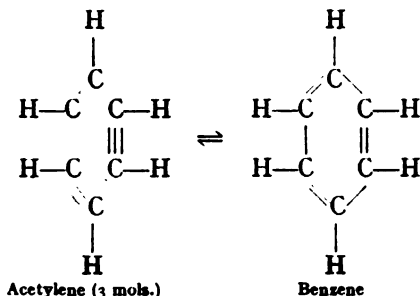
$\text{R} = \text{OH}$. H.OH = water, which cannot be directly oxidised to hydrogen peroxide HO.OH ; whence $-\text{OH}$ belongs to the first class.

$\text{R} = \text{NO}_2$. H.NO_2 = nitrous acid, which is readily oxidised to nitric acid HO.NO_2 ; whence $-\text{NO}_2$ belongs to the second class.

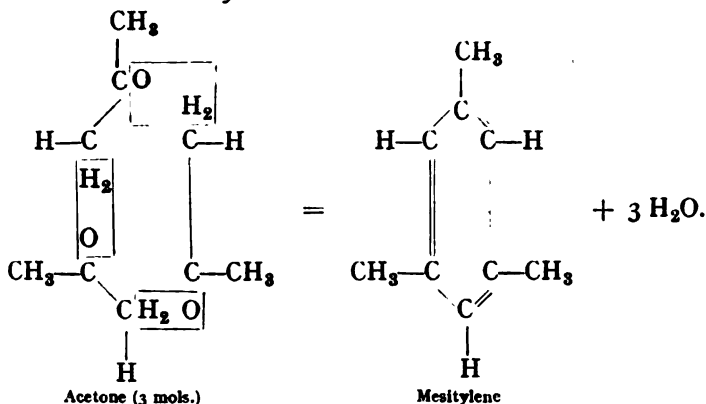
As will be seen, this rule is only empirical, and indeed in some cases is little more than a quibble; nevertheless it is a valuable substitute for memorisation, and it is probable that some as yet undiscovered fundamental principle underlies it.

TRANSITIONS BETWEEN THE ALIPHATIC AND AROMATIC SERIES

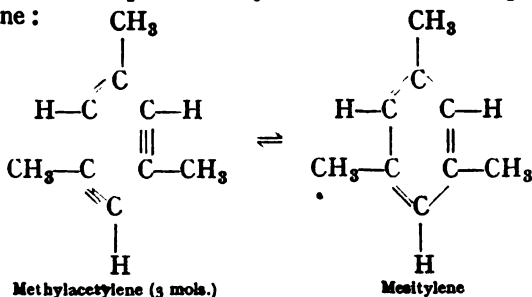
A few reactions are known by which compounds of the benzene series can be produced from aliphatic compounds, and *vice versa*. The simplest of these is the formation of benzene itself by polymerisation of acetylene. When acetylene is passed through a heated tube, three molecules unite with formation of benzene. This is not a quantitative reaction; the product issuing from the tube contains both benzene and acetylene. The reverse effect is brought about by passing the vapour of benzene through a red-hot tube, acetylene being formed by disruption of the benzene molecule. We may thus regard the action of heat on benzene and on acetylene as producing an equilibrium mixture in the sense of the balanced equation:



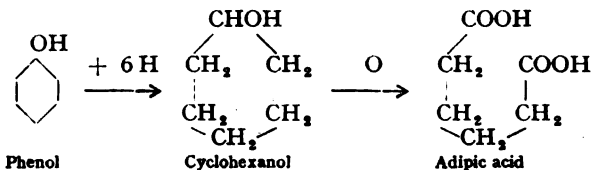
Another example of the formation of a derivative of benzene from a purely aliphatic compound is the condensation of acetone by the agency of sulphuric acid, with production of a trimethylbenzene called *mesitylene* :



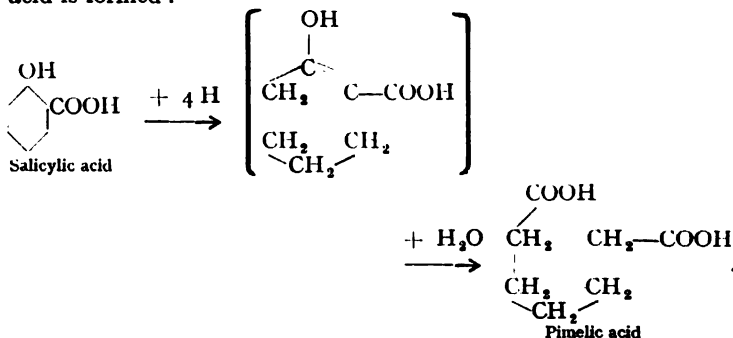
Mesitylene is also produced by the action of heat upon methylacetylene :



Convincing examples of the transition of aromatic to aliphatic compounds are afforded by the catalytic reduction of phenol to its hexahydro derivative, cyclohexanol, which on oxidation yields the straight-chain aliphatic dicarboxylic acid adipic acid :



and by the action of sodium upon a boiling solution of salicylic acid (*o*-hydroxybenzoic acid) in amyl alcohol, whereby pimelic acid is formed :



Certain other transitions between aliphatic and aromatic series have been studied, but the above examples are sufficient to indicate the reality of such changes, and to afford additional evidence of the correctness of our views with regard to the structure of benzene and its derivatives.

CHAPTER XXV

BENZENE AND ITS HOMOLOGUES

THE chief source of benzene and its homologues is **coal-tar**. When coal is strongly heated in a retort in the absence of air, it undergoes profound alteration, giving off an inflammable gas (coal gas), a mixture of condensible liquids (water and coal-tar), and a non-volatile residue (coke), consisting principally of elemental carbon and earthy matter. The coal gas, after passing through vertical condensers which remove the tar, is led through purifiers which remove hydrogen sulphide and ammonia, and is finally stored over water in gasometers. The tar, which forms a layer floating on the condensed water, is separated and distilled, while from the watery layer ammonia and other bases can be recovered.

In working up the coal-tar, the first procedure is a simple distillation; a considerable portion of this tar is not volatile, and remains in the retort as a black, fusible, amorphous mass. This is *pitch*. The next operation is to treat the distillate successively with alkali, which removes acidic substances (principally phenols), and with mineral acid, which removes basic substances. The neutral residue is thereupon submitted to fractional distillation, by which it is divided into four fractions:

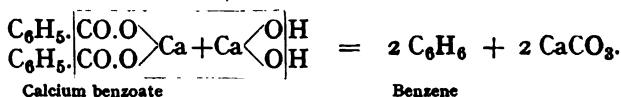
- I. Light oil, which passes over below 150° . This contains benzene, toluene, the xylenes, and some other homologues of benzene.
- II. Middle oil, which passes over between 150° and 220° , and
- III. heavy oil, which boils up to 270° . Both contain a large proportion of naphthalene (p. 411).
- IV. Anthracene oil, which boils from 270° up to about 400° , contains anthracene (p. 417), which crystallises on cooling.

In some processes, the tar is not at first treated with alkali and acid, and in this case the middle oil contains a considerable proportion of phenol and its homologues. For this reason it is sometimes also termed "carbolic oil," and it is from this fraction that the phenols are removed by treatment with alkali.

At this point we need only consider the treatment of the first fraction, the "Light oil." This is again fractionally distilled, a fractionating still-head—as in the manufacture of alcohol—being employed. By this means pure benzene, pure toluene, and a mixture of the isomeric xylenes, can be isolated.

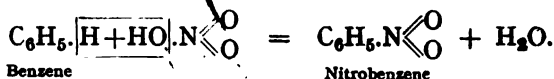
Benzene C_6H_6 is a colourless liquid, which boils at 80° and possesses a characteristic odour. It resembles all other hydrocarbons in being insoluble in, and lighter than, water. Benzene is readily inflammable, and burns with a smoky flame. On cooling, it solidifies to a crystalline mass which melts at 5° .

It may be prepared by distilling the calcium salt of benzoic acid with calcium hydroxide, or better, with soda-lime. This mode of preparation is parallel to the formation of methane by distillation of a mixture of sodium acetate and sodium hydroxide (p. 76):



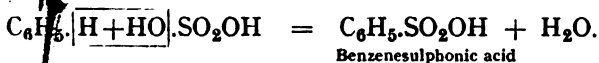
Its formation by polymerisation of acetylene and dehydrogenation of cyclohexane have already been mentioned (pp. 304, 317). In practice, however, coal-tar forms the exclusive source of benzene.

Benzene is stable towards oxidising agents. On treatment with concentrated nitric acid (or preferably a mixture of concentrated nitric acid and sulphuric acid) *nitrobenzene* is produced:

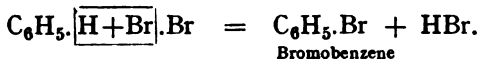


This action is termed *nitration*.

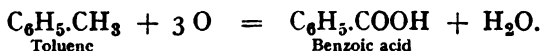
On heating with concentrated sulphuric acid alone, *sulphonation* takes place, *benzenesulphonic acid* being formed :



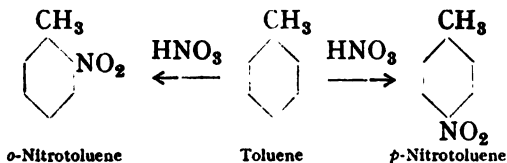
On treatment with halogens, as for instance bromine, substitution occurs :



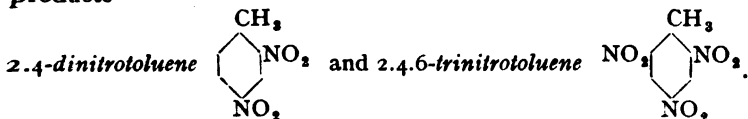
Toluene $C_6H_5.CH_3$ is a liquid resembling benzene in general properties. It boils at 110° , and solidifies at -93° . On treatment with oxidising agents, as for instance aqueous chromic acid or alkaline permanganate, the methyl group is oxidised, whereby benzoic acid is formed :



Toluene, like benzene, may be brominated, nitrated, sulphonated, and so on. Unlike benzene, it yields a mixture of mono-substitution-products; thus on nitration toluene is converted into a mixture of approximately equal quantities of *ortho*- and *para*-nitrotoluenes:



These two nitrotoluenes, on further nitration, both yield the same products—

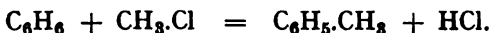


Toluene may be synthesised by the action of sodium upon a mixture of methyl iodide and bromobenzene or iodobenzene. This, the *Fittig* reaction, is parallel to the Wurtz synthesis

of propane from a mixture of ethyl iodide and methyl iodide (p. 12) :



Another synthesis can be brought about by the *Friedel and Crafts* reaction : on passing methyl chloride into a hot mixture of benzene and anhydrous aluminium chloride, toluene is produced, with elimination of hydrogen chloride :



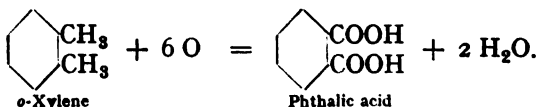
The aluminium chloride is necessary to the reaction, as it forms with the benzene an intermediate double compound which is then decomposed by the methyl chloride. On continuing this reaction, further hydrogen atoms in the benzene are replaced by methyl groups, yielding dimethylbenzenes, trimethylbenzenes, and so on. Such secondary reactions do of course not take place in the Fittig synthesis.

The **xylenes**, or *dimethylbenzenes*, $\text{C}_6\text{H}_4(\text{CH}_3)_2$ are three in number, the methyl groups in the three individuals standing respectively in the *ortho*, *meta*, and *para* positions.

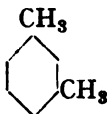
o-Xylene



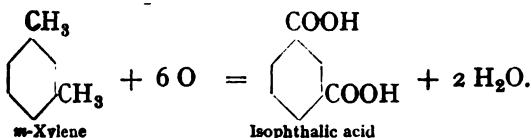
boils at 142° , and solidifies at -28° . In general properties it resembles toluene ; on oxidation it yields *phthalic acid*, or benzene-*ortho*-dicarboxylic acid (p. 397) :



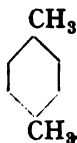
m-Xylene



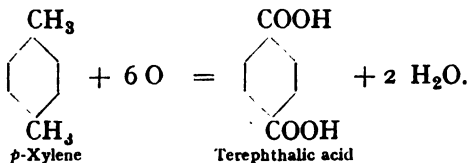
boils at 139° and solidifies at -53° . On oxidation it yields *isophthalic acid* (p. 399) :



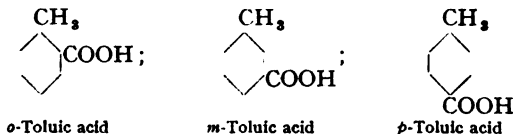
p-Xylene



melts at 13° and boils at 138° . On oxidation it yields *terephthalic acid* (p. 399) :

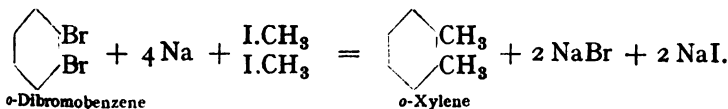


The three xylenes can, by partial oxidation, be converted into the three *toluic acids* (p. 295) respectively :



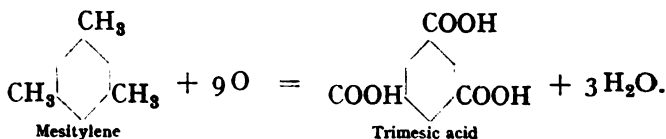
These toluic acids, on heating with soda-lime, lose carbon dioxide and yield toluene. This is parallel to the production of benzene from benzoic acid (p. 320).

The three xylenes may be synthesised by the Fittig reaction from the three corresponding dibromobenzenes. For example :

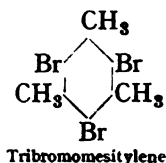
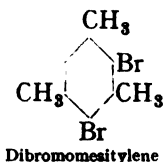
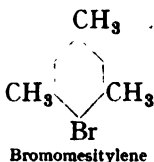


Mesitylene, or 1.3.5-trimethylbenzene, is of interest in that it is formed in the condensation of acetone by means of sulphuric

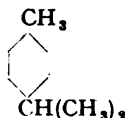
acid (p. 317). It boils at 165°. On oxidation it yields the tricarboxylic acid *trimesic acid* :



On treatment with substituting agents (bromination, nitration, etc.) it yields only one mono-, one di-, and one tri-substituted derivative :



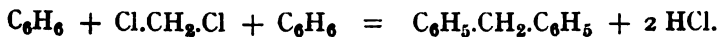
Cymene, or 1-methyl-4-isopropylbenzene,



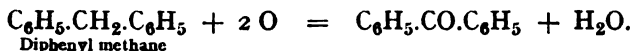
is, among the higher homologues of benzene, of especial interest, since it occurs naturally as a constituent of many essential oils, such as the oil of eucalyptus. It also has been shown to be chemically closely related to many of the *terpenes*, or hydrocarbons of the turpentine class. It is a liquid boiling at 175°. On mild oxidation with nitric acid, the isopropyl group is the first to be attacked, *p*-toluic acid being formed; on more vigorous oxidation, terephthalic acid is produced. For this reason, benzene-*para*-dicarboxylic acid is called *terephthalic acid*, to signify its connection with the *terebines*, or turpentine hydrocarbons.

It was mentioned above that toluene can be synthesised by the *Friedel and Crafts* reaction, by treating a mixture of benzene and aluminium chloride with methyl chloride. If, in place of methyl chloride, methylene chloride CH_2Cl_2 be caused to react with this mixture, a hydrocarbon containing two phenyl

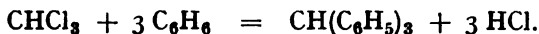
radicles attached to one carbon atom is produced ; this is **diphenylmethane** :



It is a colourless solid, melting at 23° and boiling at 261° . On oxidation it is converted into *benzophenone* (*diphenyl ketone*, p. 390) :



Similarly, if a mixture of benzene and aluminium chloride be treated with chloroform, **triphenylmethane** is produced :

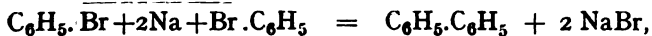


This is a colourless solid, melting at 92° . It is of especial theoretical interest, since it is the parent hydrocarbon of an important class of dyestuffs, some of which will subsequently be discussed. On oxidation it yields the corresponding alcohol, *triphenylcarbinol* :

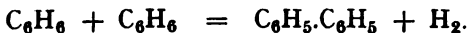


Tetraphenylmethane $\text{C}(\text{C}_6\text{H}_5)_4$ is, contrary to expectation, not produced by the action of carbon tetrachloride upon a mixture of benzene and aluminium chloride. It has, however, been prepared by a less direct method. It is a solid which melts at 272° .

A hydrocarbon consisting of two phenyl radicles directly united can be prepared by treating bromobenzene or iodobenzene with sodium. This is **diphenyl** :



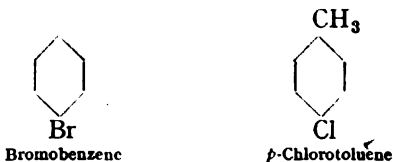
a colourless solid, melting at 70° , boiling at 254° . It is also produced by passing the vapour of benzene through a heated tube :



CHAPTER XXVI

HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES

WE shall first consider the halogen substitution-products of benzene itself, since these are typical of all aryl halides. This term "aryl" is employed to indicate a radicle consisting of a simple or substituted benzene nucleus, and is parallel to and distinct from the term "alkyl." In an aryl halide, the halogen atom must replace a hydrogen atom attached to one of the nuclear carbon atoms. Examples of aryl halides are :

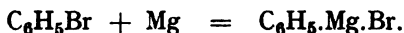


In these cases, the *phenyl* ($\text{C}_6\text{H}_5\text{—}$) and *tolyl* ($\text{CH}_3\cdot\text{C}_6\text{H}_4\text{—}$) groups are aryl radicles.

The question of isomerism among the halogen-substituted derivatives of benzene has already been discussed (p. 306). One, and only one, monohalogen derivative is known in each case—one fluorobenzene, one chlorobenzene, one bromobenzene, one iodobenzene. In the disubstituted benzenes we have the three isomers of each class,—*ortho*, *meta*, and *para*.

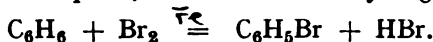
Aryl halides differ from alkyl halides in one notable particular: the halogen atoms cannot be removed from them in the way that they can be removed from alkyl halides. On treating them with reagents—such as boiling alcoholic potash—which remove the halogen from alkyl halides, no reaction takes place. It is

therefore impossible to bring about with aryl halides the majority of metathetical changes, described on p. 96, the halogen atom remains stubbornly attached to the aromatic nucleus. Ammonia, sodium sulphide, potassium cyanide, are thus entirely without action, even on prolonged heating. The only important reactions which aryl halides can be made to undergo are the elimination of halogen by means of sodium (Fittig reaction, p. 321), and the formation of organo-magnesium halides (Grignard's reagents, p. 235). An example of the latter reaction is the production of phenyl magnesium bromide by the interaction of magnesium and bromobenzene in ethereal solution :



In general behaviour aryl halides resemble the aromatic hydrocarbons. They can be sulphonated and nitrated, yielding isomeric derivatives, just as do the homologues of benzene.

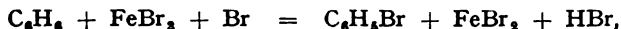
There are three general methods of preparing halogen substituted derivatives of benzene. The first of these is direct substitution. If benzene be treated with chlorine or bromine in presence of a small quantity of metallic iron or aluminium, substitution takes place, with evolution of hydrogen halide :



The metal acts catalytically as a " halogen carrier." The following explanation has been put forward to account for this effect in the case of iron :—the bromine first combines with the iron to form ferric bromide :



this ferric bromide is, during the act of bromination, reduced to ferrous bromide :



which unites at once with more bromine, ferric bromide being regenerated :



An alternative hypothesis is that the ferric or aluminium halide forms a loose addition-product with the benzene, such as $\text{C}_6\text{H}_6\text{.FeBr}_3$, and that this double compound is more easily attacked by bromine than is benzene alone. This would be parallel to the

action of the aluminium chloride in the Friedel-Crafts reaction (p. 322).

The second general method is an indirect reaction, depending on the replacement of the amino group in primary amines, such as aniline $C_6H_5.NH_2$, by a halogen atom. This is the Sandmeyer reaction; it will be described later (p. 375), after considering the properties of the amino derivatives of benzene.

The third general method consists in the replacement of the hydroxyl group in phenols, for example phenol itself C_6H_5OH (p. 337), by treatment with phosphorus pentachloride. The parallel to this in the aliphatic series has already been mentioned (p. 95).

The corresponding derivatives of iodine—the aryl iodides—can be prepared only by indirect methods, the chief of which is the Sandmeyer reaction.

Chlorobenzene C_6H_5Cl is prepared by passing dry chlorine into warm benzene, in presence of a small quantity of iron filings, until the total weight of the reaction-mixture corresponds with the change $C_6H_6 \rightarrow C_6H_5Cl$. The product is then fractionally distilled. Chlorobenzene is a colourless liquid, boiling at 132° .

If the passage of chlorine be continued after this point has been reached, **dichlorobenzenes**—a mixture of the *para* compound



with a smaller proportion of the *ortho* isomer

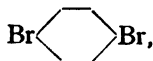


—are produced.

Chlorobenzene, on nitration, yields a mixture of approximately equal quantities of *ortho* and *para* nitrochlorobenzenes (p. 352).

Bromobenzene C_6H_5Br is prepared in the same way as chlorobenzene, by allowing one molecular proportion of dry bromine to react gradually with one molecular proportion of

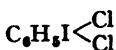
benzene. It is a colourless liquid, boiling at 157° . With two molecular proportions of bromine, the chief product is **p-dibromobenzene**



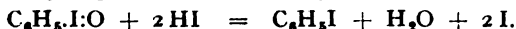
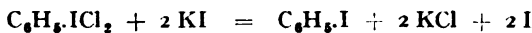
a white solid, melting at 87° and boiling at 219° .

Iodobenzene $\text{C}_6\text{H}_5\text{I}$, prepared by the Sandmeyer reaction (p. 375), is a colourless liquid boiling at 188° .

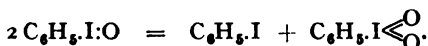
An interesting property of aryl iodides is their faculty of forming derivatives of tervalent and quinquivalent iodine. On passing chlorine into iodobenzene, a yellow crystalline *dichloride*



is formed. This, on treatment with aqueous sodium hydroxide, yields *iodosobenzene* $\text{C}_6\text{H}_5\text{I}:\text{O}$. Both of these substances are somewhat unstable, and thus behave as oxidising agents, liberating iodine from potassium iodide or hydrogen iodide :



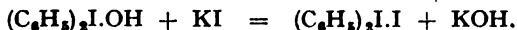
On standing, or, more rapidly, on gently warming, iodosobenzene is converted into iodobenzene and *iodoxybenzene* :



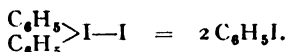
Another interesting class of tervalent iodine compounds is found in the *iodonium bases*. If moist silver oxide be allowed to interact with an equimolecular mixture of iodosobenzene and iodoxybenzene, *diphenyl iodonium hydroxide* is formed :



These iodonium hydroxides are strong bases, resembling the hydroxides of quaternary ammonium (p. 202) or tertiary sulphonium (p. 213) compounds. Diphenyl iodonium iodide is a sparingly soluble salt, which is precipitated on adding potassium iodide to the iodonium hydroxide :

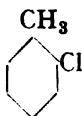


On heating, it readily breaks down into pure iodobenzene :

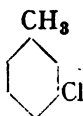


CHLORINE DERIVATIVES OF TOLUENE

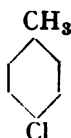
In accordance with the theory, there exist three isomeric chlorotoluenes:



o-Chlorotoluene
B.P. 157°

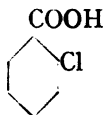


m-Chlorotoluene
B.P. 162°

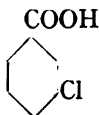


p-Chlorotoluene
B.P. 162°

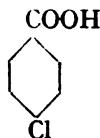
When dry chlorine is passed into toluene, in the presence of a "halogen carrier," in the cold, and in absence of direct sunlight, a mixture of chlorotoluenes is produced. These are true halides, and resemble chlorobenzene in chemical character. On oxidation, these three chlorotoluenes yield the three corresponding isomeric chlorobenzoic acids:



o-Chlorobenzoic acid
M.P. 138°



m-Chlorobenzoic acid
M.P. 153°



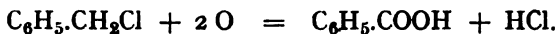
p-Chlorobenzoic acid
M.P. 234°

which may readily be distinguished by their different melting-points.

Now in toluene there are three hydrogen atoms which differ from the other five, namely those attached to the methyl group. Substitution of one of these, therefore, would lead to a chloro-derivative of toluene in which the chlorine atom is not directly attached to the aromatic nucleus and we might expect such a derivative to partake of the character of an alkyl halide. This is in fact the case.

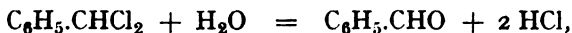
When chlorine is passed into boiling toluene in presence of direct sunlight, a vigorous reaction takes place, hydrogen chloride being evolved. The first product of this reaction is a liquid of the empirical formula C_7H_7Cl , boiling at 178° . On oxidation,

it yields benzoic acid ; the chlorine atom, therefore, must be attached to the carbon atom of the methyl group in toluene :

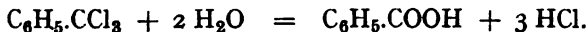


This substance is termed **benzyl chloride**. It is not an aryl halide, for the chlorine atom is not directly attached to the benzene nucleus, and its behaviour is that of an alkyl halide. The chlorine is readily removed, and benzyl chloride undergoes all the metathetical reactions of alkyl halides. With potassium hydroxide it yields benzyl alcohol (p. 342) $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$; with ammonia it yields benzylamine (p. 364) $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}_2$; it yields a nitrile $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CN}$ on treatment with potassium cyanide ; and so on.

On further chlorination, **benzal chloride** $\text{C}_6\text{H}_5\cdot\text{CHCl}_2$ and **benzotrichloride** $\text{C}_6\text{H}_5\cdot\text{CCl}_3$ are produced. These substances are liquids which boil at 204° and 213° respectively. Like the corresponding derivatives of methane (*cf.* methylene chloride, chloroform, pp. 101, 102) benzal chloride is converted by hydrolysis into an aldehyde, benzaldehyde (p. 384) :



while benzotrichloride yields benzoic acid (p. 391) on hydrolysis :

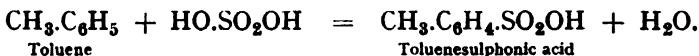
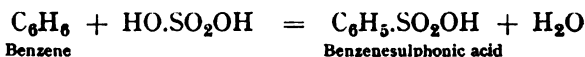


Hydrolysis takes place rather more readily with these substances than it does with the corresponding purely aliphatic compounds.

CHAPTER XXVII

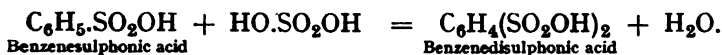
AROMATIC DERIVATIVES OF SULPHUR

THE reaction termed *sulphonation* has already been referred to as being a characteristic reaction undergone by aromatic compounds. Sulphonation is a condensation whereby a nuclear hydrogen atom of the benzene derivative and one of the hydroxyl groups of sulphuric acid are eliminated :

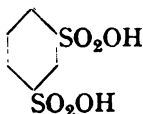


The products—**sulphonic acids**—are strongly acid substances, as a rule soluble in water and alcohol, and insoluble in ether. Typical of these is **benzenesulphonic acid** $\text{C}_6\text{H}_5.\text{SO}_2\text{OH}$, which is prepared by heating a mixture of benzene and concentrated sulphuric acid until the benzene has completely entered into solution. The reaction mixture is diluted and neutralised with calcium or barium carbonate, whereby the unchanged sulphuric acid is precipitated as calcium or barium sulphate, the salt of benzenesulphonic acid remaining in solution. Lead carbonate may also be employed for the purpose. The salt of the sulphonic acid is obtained by evaporating to dryness and recrystallising from water. In order to obtain the free sulphonic acid, exactly the requisite amount of sulphuric acid is added, and the filtered solution evaporated to dryness. It is preferable to decompose the lead salt by means of hydrogen sulphide.

On continuing the sulphonation, a disulphonic acid is produced :



The *meta* isomer



is exclusively formed. The formation of *meta* compounds is characteristic of all reactions by which substituents are introduced into sulphonic acids ; *meta* substituted derivatives are always produced, neither the *ortho* nor the *para* isomers being simultaneously formed. This fact we express by saying that the sulphoxyl ($-\text{SO}_2\text{OH}$) group has a *meta* directing influence.

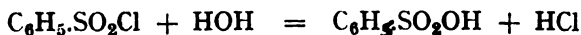
Sulphonic acids resemble carboxylic acids in many particulars, though as a rule they are stronger acids (more completely ionised in solution). On treatment with phosphorus pentachloride they are converted into the corresponding sulphonic chlorides or **sulphochlorides** :



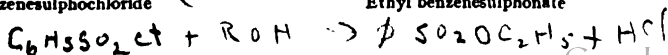
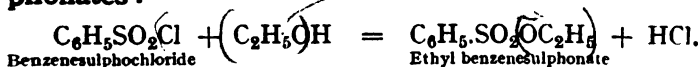
It is more convenient to prepare sulphochlorides from metallic salts of sulphonic acids, such as sodium benzenesulphonate :



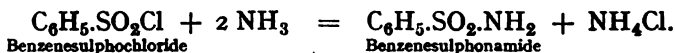
These sulphonic chlorides are more stable towards water than are the carboxylic chlorides ; only on heating does the reaction :



proceed rapidly. This reaction forms a method for preparing pure sulphonic acids. Sulphochlorides react slowly on the alcohols in the cold, yielding sulphonic esters or **alkyl sulphonates** :

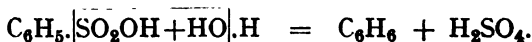


On treatment with ammonia or ammonium carbonate, they are converted into **sulphonamides** :

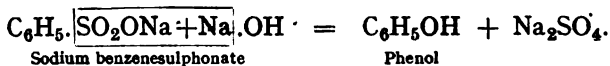


Aromatic sulphonamides are crystalline solids, possessing sharp and characteristic melting-points. A notable feature is their acidic character ; they form metallic salts in which an atom of an alkali metal replaces one of the amino hydrogen atoms : $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NHNa}$. For this reason sulphonamides, which as a rule are almost insoluble in water, dissolve in aqueous alkalis. The same is the case with sulphonyl derivatives of primary amines such as benzenesulphonyl-methylamine $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_3$. Sulphonamides derived from secondary amines, such as benzenesulphonyl-dimethylamine $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{N}(\text{CH}_3)_2$, cannot form such salts and are therefore insoluble in alkali.

The sulphonic acids themselves are for the most part hygroscopic crystalline solids. They do not melt on heating, but decompose at a high temperature. On heating sulphonic acids with concentrated hydrochloric acid at about 180° , or with 70 per cent. aqueous sulphuric acid at this temperature in a current of superheated steam, the sulfoxyl radicle is split off, an atom of hydrogen taking its place :



If, on the other hand, a metallic sulphonate be fused with caustic alkali, a sulphite is formed, and a hydroxyl group takes the place of the sulfoxyl group. This is a general method for preparing *phenols* (p. 340) :



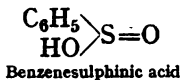
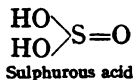
Benzenesulphochloride is a colourless liquid, which is insoluble in water. It decomposes on heating under atmospheric pressure, but boils under 10 mm. pressure at 120° , and, on cooling, solidifies to a solid melting at 14° . It is readily soluble in ether.

Benzenesulphonamide is a white crystalline solid which is slightly soluble in hot water, readily so in alcohol or ether, and melts at 150° .

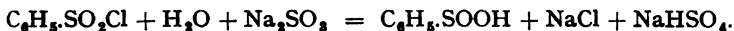
Sulphonic acids and their derivatives may be regarded as being akin to sulphuric acid, in the sense that the sulphur atom is in its sexavalent state :



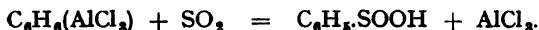
Substances similarly related to sulphurous acid are known ; these are the **sulphinic acids** :



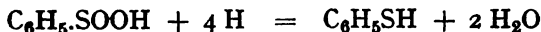
Sulphonic acids themselves resist the action of reducing agents, but the corresponding sulphochlorides are amenable to reduction. On treatment with sodium sulphite, sulphochlorides are readily reduced to sulphinic acids :



Little need be here noted concerning sulphinic acids ; they are strong acids, and may be readily reoxidised to sulphonic acids, from which they differ in being susceptible to the action of reducing agents. They may also be prepared by the action of sulphur dioxide upon mixtures of aromatic hydrocarbons and aluminium chloride :



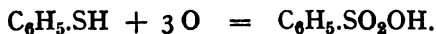
On vigorous reduction, as with tin and hydrochloric acid, sulphochlorides and sulphinic acids are converted into the corresponding aromatic mercaptans or **thiophenols** :



Thiophenols possess the same general properties as aliphatic mercaptans (p. 209). On mild oxidation they are converted into **disulphides** :



on more powerful oxidation they yield sulphonic acids :



Aromatic **sulphides** are also known. Such is phenyl sulphide $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_5$, which is produced by the interaction of hydrogen sulphide or thiophenol and diazobenzene (p. 375). These sulphides are similar in properties to the aliphatic sulphides (p. 211) : on mild oxidation they yield the corresponding **sulphoxides** (cf. such as phenyl sulphoxide) $\text{C}_6\text{H}_5\cdot\text{SO}\cdot\text{C}_6\text{H}_5$, with powerful oxidising agents they are converted into **sulphones** (cf. pp. 213, 214), such as phenyl sulphone $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$.

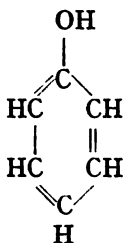
CHAPTER XXVIII

HYDROXY DERIVATIVES OF BENZENE AND TOLUENE

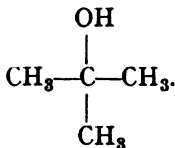
It has already been pointed out that the hydrogen atoms attached to nuclear carbon atoms in aromatic compounds can be replaced by hydroxyl groups. The resulting hydroxy-compounds, known by the generic term *phenols*, resemble in many of their properties the corresponding aliphatic hydroxy-compounds, the alcohols.

The prototype of the phenols is the simplest example, hydroxy-benzene, known as **phenol**, or popularly as *carbolic acid* C_6H_5OH . In the matter of homology and isomerism the conditions obtaining in the hydroxyl derivatives of benzene and its homologues are identical with those enumerated for the aromatic halogen derivatives. Only one monohydroxybenzene is known; three (*ortho*, *meta* and *para*) dihydroxybenzenes; four monohydroxytoluenes, corresponding with the three chlorotoluenes and benzyl chloride respectively. Similar relations hold throughout the series.

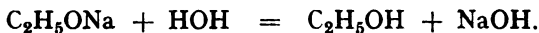
Phenols, whilst possessing, in a general way, chemical properties resembling those of the alcohols, differ markedly in some particulars. In the first place, oxidation of a phenol does not lead to a carboxylic acid, an aldehyde, or a ketone; on oxidation, the structure of the phenol molecule is destroyed. A parallel to this in the aliphatic series is to be found in the tertiary alcohols (p. 107), which on oxidation are converted into substances containing fewer carbon atoms. And indeed we may regard phenol itself in this light as a tertiary alcohol:



It will be noted that the remaining valencies of the carbon atom to which the hydroxyl group is attached are all directly united with carbon atoms, as is the case in the tertiary alcohols, such as tertiary butyl alcohol (p. 117) :



A more striking feature of phenols is one, however, which they do not share in common with aliphatic tertiary alcohols : they possess well-marked acidic properties. Aqueous solutions of phenols, even when dilute—for many phenols are only sparingly soluble in water—red den litmus. Moreover, phenols which dissolve but slightly in water, dissolve readily in aqueous sodium or potassium hydroxide solutions. If equimolecular proportions of phenol and sodium hydroxide be mixed in aqueous solution, and the solution evaporated to dryness, a salt of composition corresponding with the formula $\text{C}_6\text{H}_5\text{ONa}$ is obtained. This is called *sodium phenoxide*, and corresponds to the far less stable sodium ethoxide $\text{C}_2\text{H}_5\text{ONa}$ (p. 109) derived from ethyl alcohol. The difference between the two is exemplified by the following fact : if an aqueous solution of sodium ethoxide be distilled, ethyl alcohol passes into the distillate :

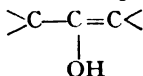


An aqueous solution of sodium phenoxide, on the other hand,

loses no phenol on boiling, although phenol is readily volatile with steam in the absence of alkali.

Another characteristic property of phenols is their faculty for developing intense colours—blue, violet, green, etc., with dilute solutions of ferric chloride. These colours are due to the formation of complex iron salts.

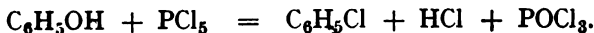
It is interesting here to recall the fact that ketonic substances, such as ethyl acetoacetate, which are capable of existing in an enolic form (p. 261): $\text{CH}_3\text{C}(\text{OH})\text{:CH}\cdot\text{COOC}_2\text{H}_5$, also develop characteristic colours with ferric chloride and from sodium salts. In structure we can perceive analogies between phenols and such enolic substances: both contain the grouping:



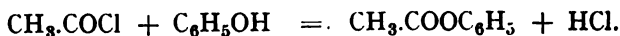
Phenols are, in spite of these well-defined acidic properties, only weak acids. Their salts are decomposed, not only by strong mineral acids, and by carboxylic acids such as acetic acid, but in fact by so weak an acid as carbonic acid:



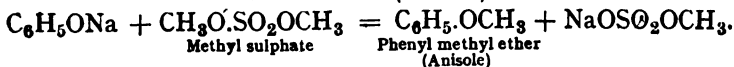
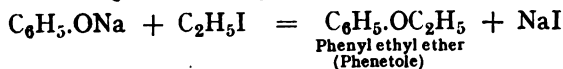
Of the remaining properties of phenols the majority are those common to aliphatic alcohols: on treatment with phosphorus pentachloride they yield chloro-compounds:



whilst with carboxylic acid chlorides they yield esters:

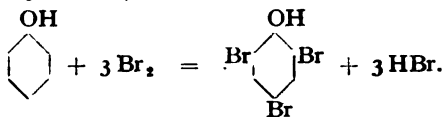


$\text{CH}_3\text{COCl} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Phenyl acetate}$
 Their sodium or potassium salts, on treatment with alkyl halides or inorganic esters, yield ethers:



We have just seen how the aromatic nucleus affects the properties of the phenolic hydroxyl group, rendering it more acidic in character than an alcoholic hydroxyl group. The hydroxyl group in turn has a marked effect on the chemical character of

the aromatic radicle, causing certain of the hydrogen atoms attached to nuclear carbon atoms to be more amenable to substitution by other atoms or groups. Thus phenol, on treatment with bromine water, at once yields 2.4.6-tribromophenol (see below) :

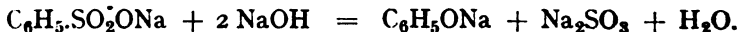


It will be recalled that benzene, on the other hand, can be brominated only by dry bromine in presence of a halogen carrier. Similarly, nitrophenols (p. 353) are produced by treatment of phenol even with dilute nitric acid, and are more readily sulphonated by the action of concentrated sulphuric acid.

The principal source of phenols is, like that of benzene and its homologues, coal tar. The crude tar, after one distillation, is treated with sodium hydroxide solution ; in this way the phenols are brought into aqueous solution, and can be separated from the remainder of the tar. This alkaline solution is then acidified with sulphuric acid, whereby the phenols are liberated and these are then separated by fractional distillation. The chief products thus obtainable are *phenol* itself $\text{C}_6\text{H}_5\text{OH}$, and the isomeric *cresols* $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, which are the three phenols derived from toluene. The mixture of phenols so obtained is employed as crude "carbolic acid" for disinfectant and other purposes.

Other general methods of preparing phenols are :

(1) By fusing aromatic sulphonates, such as sodium benzene-sulphonate, with alkali (p 334) :



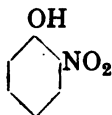
The fused mass is allowed to cool, dissolved in water, and the alkali neutralised with acid, whereby the phenol is set free from its sodium salt.

(2) By treatment of a boiling solution of an aromatic primary amine, such as aniline (p. 360), in dilute mineral acid with nitrous acid or sodium nitrite ; this reaction is in principle analogous to the behaviour of aliphatic primary amines with nitrous acid (p. 201) :

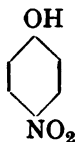


The mechanism of this reaction will be more fully discussed later (p. 373).

Phenol (*benzophenol*) C_6H_5OH is a colourless crystalline substance which melts at 42° and boils at 183° . It is somewhat soluble in water, and possesses a marked and characteristic odour. In the pure state or in concentrated solution it attacks the skin; in dilute solution it is employed as an antiseptic. It is very poisonous. As above stated, phenol is readily attacked by substitutive agents, and yields, with chlorine or bromine, the 2,4,6-trichloro- or -tribromo- derivatives. With nitric acid it yields firstly a mixture of *ortho* and *para* mononitrophenols (p. 353) :

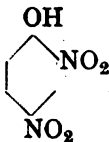


o-Nitrophenol

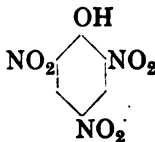


p-Nitrophenol

On further substitution, 2,4-dinitrophenol, and ultimately 2,4,6-trinitrophenol or picric acid (p. 354) :

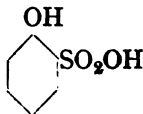


2,4-Dinitrophenol

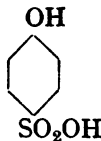


2,4,6-Trinitrophenol

On treating phenol with concentrated sulphuric acid, *ortho* and *para* phenolsulphonic acids are produced :



o-Phenolsulphonic acid

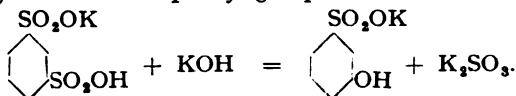


p-Phenolsulphonic acid

The corresponding *meta* isomer is not formed.

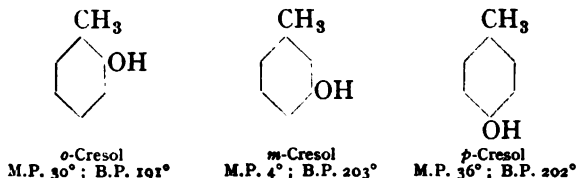
The conditions of working determine, to a great extent, which of the isomers is formed. If the reaction mixture is kept cool, the chief product is the *ortho* acid; on carrying out the reaction at

100-110°, *p*-phenolsulphonic acid is exclusively produced. The *meta* isomer can only be produced indirectly. By heating *m*-benzenedisulphonic acid with concentrated potassium hydroxide to 170-180°, only one of the sulphonyl groups is eliminated :

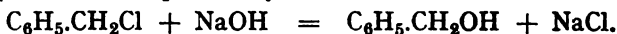


On addition of a drop of dilute aqueous ferric chloride to a dilute solution of phenol in water, an intense violet colour is developed.

The **cresols** $\text{CH}_3\cdot\text{C}_6\text{H}_4\text{OH}$, which are the phenols derived from toluene, are three in number. In chemical character they closely resemble benzophenol :

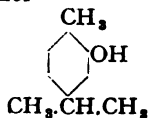


The fourth isomer, in which the hydroxyl group replaces one of the hydrogen atoms in the methyl group of toluene, is not a phenol, and behaves strictly as an aliphatic alcohol. This is **benzyl alcohol** $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$, which is produced by the action of aqueous alkali upon benzyl chloride :



It is a colourless, almost odourless liquid, boiling at 204°. It is a neutral substance, and its sodium derivative (prepared by the action of sodium upon dry benzyl alcohol) is, like sodium ethoxide (p. 109), hydrolysed in aqueous solution. In all respects it behaves as a primary alcohol; on oxidation it yields the corresponding aldehyde (benzaldehyde $\text{C}_6\text{H}_5\cdot\text{CHO}$, p. 384), and carboxylic acid (benzoic acid $\text{C}_6\text{H}_5\cdot\text{COOH}$, p. 391).

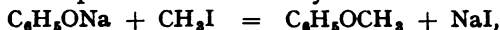
Of the higher homologues of phenol, the only one which need here be mentioned is **thymol**



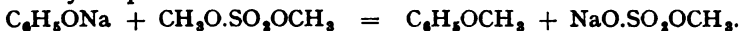
This is a phenolic hydroxy-derivative of cymene (p. 324), occurring in certain vegetable oils. It is a colourless solid, of characteristic odour. It melts at 50° and boils at 232° .

PHENOLIC ETHERS.

Alkyl ethers of phenols may be prepared by the action of alkyl halides or inorganic alkyl esters upon the alkali salts of phenols. Phenyl methyl ether, or **anisole** $C_6H_5.OCH_3$, is prepared by boiling alcoholic sodium phenoxide with methyl iodide :

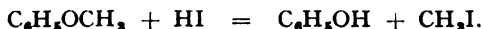


or by shaking an aqueous solution of sodium phenoxide with methyl sulphate :



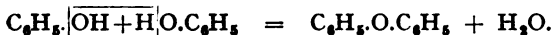
Phenyl ethyl ether, or **phenetole**, $C_6H_5.OC_2H_5$, is produced in a similar manner.

These ethers are fragrant liquids which combine in themselves the characteristic properties of aromatic hydrocarbons and aliphatic ethers. They are somewhat more readily acted upon by substituting agents than the hydrocarbons, yielding a mixture of the *ortho*- and *para*- monosubstituted derivatives. They are also more readily hydrolysed than the purely aliphatic ethers : on warming with concentrated hydriodic acid, they yield phenol and alkyl iodide :



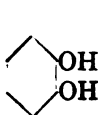
On warming with aluminium chloride they are similarly broken up, yielding alkyl chlorides.

Diphenolic ethers may, on the other hand, be synthesised by means of aluminium chloride : on heating phenol with aluminium chloride (or zinc chloride) **diphenyl ether** is produced :

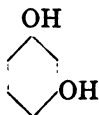


The metallic chloride acts in this case as a dehydrating agent. Such diphenolic ethers are hydrolysed neither by aluminium chloride nor by heating with hydriodic acid even to 250° .

POLYHYDROXYLIC PHENOLS resemble monohydroxylic phenols in their principal chemical attributes. The most important of these are the dihydroxylic derivatives of benzene, which, as might be anticipated, are three in number :



Catechol



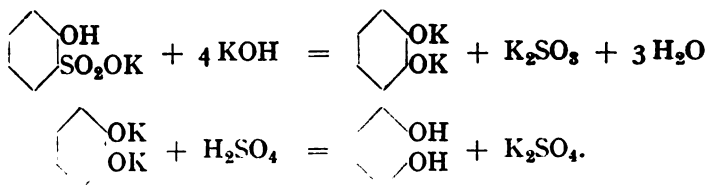
Resorcinol



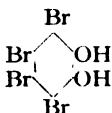
Quinol

These dihydroxylic phenols are, like the glycols (p. 128), capable of forming mono- and di-acyl esters, and mono- and di-alkyl ethers.

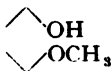
Catechol (*o-dihydroxybenzene*) is produced by the dry distillation of certain vegetable products. It may be obtained synthetically by fusing *o*-phenolsulphonic acid with potassium hydroxide :



It is a white crystalline substance, which melts at 104° and boils at about 240° . It is very soluble in water. It is more readily oxidised than the monohydroxylic phenols; an alkaline solution of catechol rapidly darkens (due to oxidation) in presence of atmospheric oxygen, and a neutral aqueous solution precipitates metallic silver from silver nitrate even in the cold. With bromine it is at once converted into tetrabromocatechol :

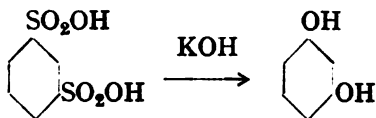


Its monomethyl ether, **guaiacol**

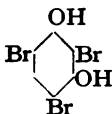


occurs in the tar formed by the dry distillation of beech-wood. It forms one of the sources of catechol, which is produced from it by heating with hydriodic acid or with aluminium chloride.

Resorcinol (*m-dihydroxybenzene*) is a substance closely resembling catechol in general properties. It may be prepared by various synthetic methods, chief of which is fusion of *m*-benzenedisulphonic acid with potassium hydroxide :

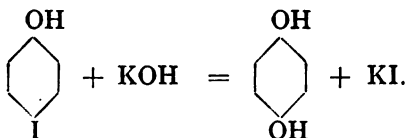


Resorcinol is a white crystalline substance, which melts at 119° and boils at 276° . It is very soluble in water, and is readily oxidised, though not quite so readily as catechol. With bromine water it at once yields tribromoresorcinol :



Characteristic of resorcinol and its homologues, in which the hydroxyl groups are situated relatively in the meta position, is their faculty of yielding dyestuffs by condensation with phthalic anhydride (p. 398). On heating a mixture of resorcinol and phthalic anhydride to 200° , a substance of complicated structure called *fluorescein* is produced (p. 441). On adding sodium hydroxide to an aqueous solution of fluorescein, a brilliant green fluorescence is developed.

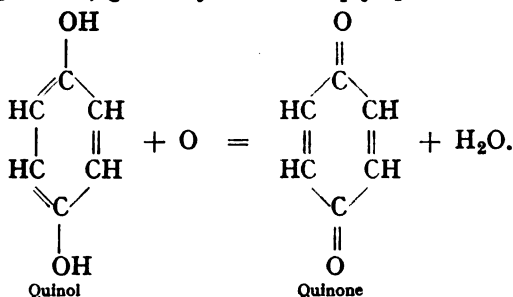
Quinol or **hydroquinone** (*p-dihydroxybenzene*) occurs naturally in small quantities in certain vegetable substances. It may also be prepared synthetically in various ways, as for instance by fusing *p*-iodophenol with potassium hydroxide :



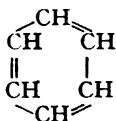
The chief method of preparation, however, is by the reduction of quinone, which will be described below.

Quinol is a colourless crystalline solid, which melts at 169° . It is very soluble in water and is even more readily oxidised than resorcinol or even catechol. For this reason it is employed as a photographic developer ; an alkaline solution of quinol forms a mild reducing agent which is capable of reducing to metallic silver the silver bromide which has been exposed to light, while leaving unaltered the silver bromide not so exposed.

On oxidation in acid solution, quinol is converted into **p-benzoquinone**, generally called simply **quinone**:



Examination of the structure of quinone shows that in this substance the benzenoid arrangement of the valencies has been fundamentally altered. At first sight it might be supposed that quinone would behave merely as an unsaturated aliphatic ketone, but the peculiar structural arrangement leads in some way to distinctive chemical and physical characteristics, just as the properties of benzene itself are not those which might be anticipated from the structure:

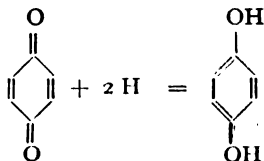


In short, the quinonoid arrangement, expressible by the ideograph:



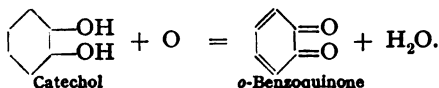
conveys with it certain ideas distinct from the conceptions of either aliphatic or benzenoid structures.

Chief of these characteristics of quinonoid substances are, firstly, their aptitude for reduction with regeneration of benzenoid compounds:



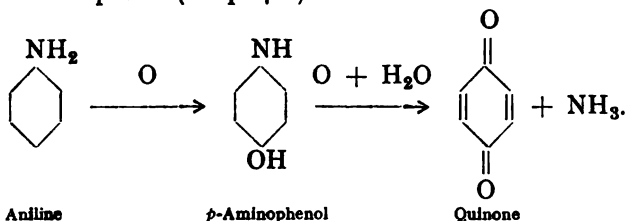
and secondly the fact that quinonoid substances are endowed with colour.

In this connection it may here be mentioned that a second class of quinones, similar in many respects, is known, namely those derived from *ortho* compounds. These also are readily reduced to compounds of benzenoid structure, and likewise possess colour. The simplest of these is *o*-benzoquinone, which can be prepared by oxidation of catechol under suitable conditions :



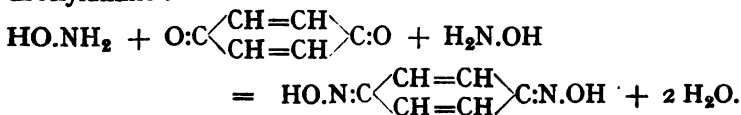
This is readily reconverted by reducing agents into catechol. As a class, *ortho* quinones are less important than *para* quinones, and need not here be further considered.

Quinone is a yellow crystalline solid, which melts at 116° and possesses a powerful and peculiar odour. It is readily obtained by oxidation of quinol, *p*-phenolsulphonic acid, and many other *para* substituted compounds. Its chief mode of preparation, however, is by the oxidation of aniline (p. 360) by means of chromic acid. This reaction probably takes place in several stages, *p*-aminophenol being produced as an intermediate compound (see p. 426) :

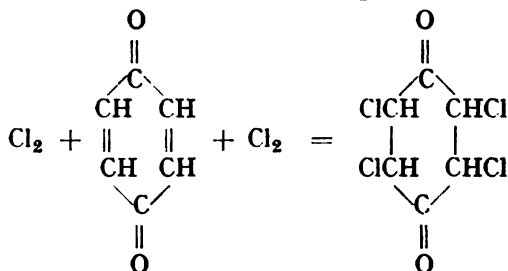


The quinone so prepared is, as above stated, readily reduced ; so readily, indeed, that it behaves as an oxidising agent. For instance, it liberates iodine from hydriodic acid.

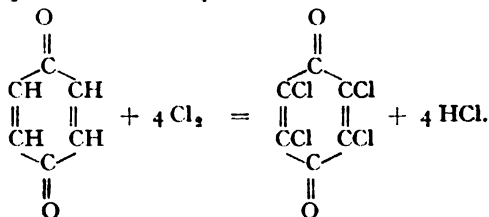
The fact that quinone contains two carbonyl groups is shown by the formation of a dioxime on treatment with hydroxylamine :



The presence of two double bonds in the molecule is shown by the fact that it forms a tetrachloro addition-product with chlorine :

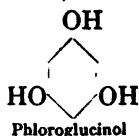
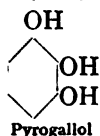


As a rule, however, chlorine acts as a substituting agent, leading to tetrachloroquinone, often termed *chloroanil* :

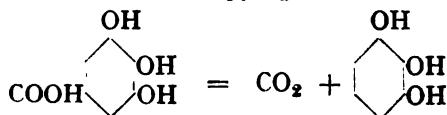


This substance is formed by the action of a mixture of potassium chlorate and hydrochloric acid upon aniline, from which fact is derived the name chloroanil.

Of the other polyhydroxylic derivatives of benzene, the more important are **pyrogallol** (1.2.3-trihydroxybenzene), and **phloroglucinol** (1.3.5-trihydroxybenzene) :

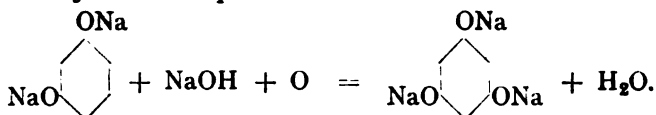


Pyrogallol is obtained by heating *gallic acid* (p. 402) which is a carboxylic acid derived from pyrogallol :



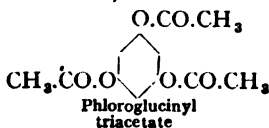
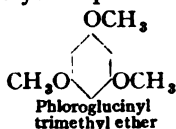
It is white crystalline substance, which melts at 132° . It is very soluble in water, and is oxidised in alkaline solution even more readily than the dihydroxy derivatives of benzene. Such a solution is employed in gas-analysis for absorbing oxygen, also as a photographic developer.

Phloroglucinol can be obtained by a variety of synthetic methods, the chief of which is the fusion of resorcinol with sodium hydroxide in presence of air :

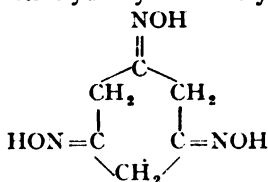


It is a colourless substance which crystallises with two molecules of water.

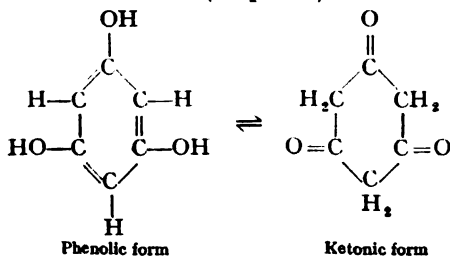
The chief interest in connection with phloroglucinol is its hermaphrodite chemical character ; it can react either as a phenol or as a ketone. On the one hand, with alkylating or acylating agents, it yields phenolic ethers and esters, such as :



On the other hand, with hydroxylamine it yields a trioxime :



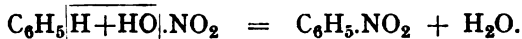
For these reasons it must be regarded as being able to behave in either of the two tautomeric (cf. p. 261) forms.



CHAPTER XXIX

AROMATIC NITRO COMPOUNDS

THE existence will be recalled of a class of aliphatic nitro compounds, the *nitroparaffins* (p. 206), the prototype of which is nitromethane CH_3NO_2 . These compounds are of no great moment; the corresponding aromatic nitro compounds, on the other hand, form an extensive and important class. Nitric acid, it will be remembered, has little or no action upon saturated aliphatic hydrocarbons, and nitroparaffins must be prepared by indirect processes; aromatic hydrocarbons differ markedly from the paraffins in reacting readily with nitric acid, yielding nitro derivatives. Thus benzene, on treatment with nitric acid, is converted into nitrobenzene:



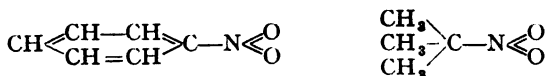
This reaction is known as *nitration*. It is frequently found expedient to employ, instead of nitric acid, a mixture of concentrated nitric and sulphuric acids; fuming nitric acid is also often employed for nitration.

The homologues of benzene also yield nitro-compounds on nitration; as, however, the properties of these homologues nitro-compounds closely resemble those of the corresponding derivatives of benzene, we shall at the outset confine our attention to those simpler compounds.

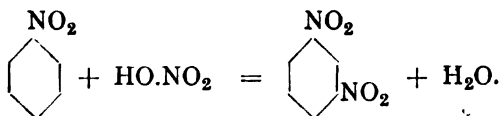
Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$ is prepared by shaking together a cold mixture of benzene and concentrated nitric and sulphuric acids. It is a faintly yellow, almost colourless, oil, boiling at 208° . When cooled, it solidifies to a crystalline mass melting at 5° . It is soluble in and heavier than water, and possesses a

powerful odour recalling that of the oil of bitter almonds, for which it is occasionally employed as a substitute or adulterant.

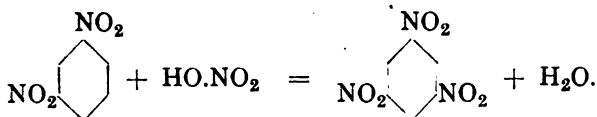
Nitrobenzene forms no metallic derivatives of the type obtainable from nitromethane. This is due to the absence of replaceable hydrogen atoms—the nitro group is attached to a carbon atom the remaining three valencies of which are bound to carbon atoms. In this respect it resembles tertiary nitrobutane :



On nitration of nitrobenzene by treatment with fuming nitric acid and concentrated sulphuric acid, *m*-dinitrobenzene is produced :



On further nitration, 1,3,5-trinitrobenzene is formed :



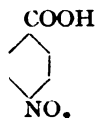
These substances are yellow solids which—especially in the case of trinitrobenzene—show a tendency to explode. On gradual heating in air, they merely take fire, but when violently struck or detonated, they decompose with explosive violence.

When toluene is nitrated under the conditions employed for preparing nitrobenzene, a mixture of equal quantities of *ortho* and *para* nitrotoluenes is produced :

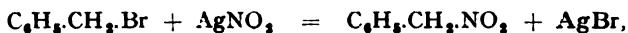


These substances closely resemble nitrobenzene in chemical properties, with the difference that they can be oxidised to the

carboxylic acids, *o*-nitrobenzoic acid and *p*-nitrobenzoic acid respectively :

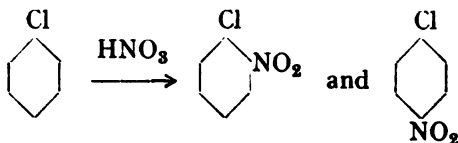


o-Nitrotoluene melts at -10° and boils at 218° ; *p*-nitrotoluene melts at 51° and boils at 234° . They are bright yellow, and resemble nitrobenzene in odour. *m*-Nitrotoluene can be obtained only by an indirect method. A fourth isomer, **phenyl-nitromethane** $C_6H_5.CH_2.NO_2$, obtained by the action of benzyl bromide upon silver nitrate :

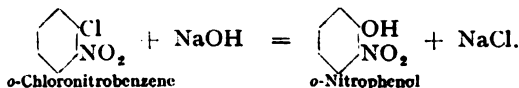


behaves in every way as an aliphatic nitro-compound.

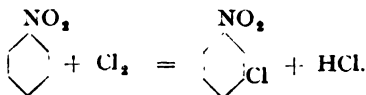
Besides hydrocarbons, other substituted derivatives of benzene and its homologues may be nitrated. Thus chloro- and bromobenzene yield mixtures of the *ortho* and *para* mono-nitro derivatives on treatment with cold fuming nitric acid :



An important feature of these compounds is their difference in chemical character from chloro- or bromobenzene. These latter, as was stated on p. 326, undergo no change on boiling with alkalis; the *ortho* and *para* nitro derivatives, on the other hand, enter into double decomposition with alkalis, yielding nitrophenols :



On nitration of chloro- and bromobenzene, the *meta* nitro derivative is not formed. This is, however, the sole product obtained by chlorination or bromination of nitrobenzene :



In this compound the reactivity of the halogen atom is of the same order as that in chloro- or bromobenzene, that is to say, halogen is not removed by boiling with alkali. We thus see that this effect of the nitro group is observed only in halogen atoms situated in the *ortho* or *para* positions relatively to the nitro group.

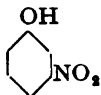
Phenols are far more readily nitrated than are the corresponding hydrocarbons, so that the nitric acid must be diluted with water for the preparation of mononitrophenols. On adding benzophenol to 25 per cent. aqueous nitric acid in the cold, a mixture of *ortho* and *para* nitrophenols is obtained. These may be separated by distillation of the resulting mixture in a current of steam—the *ortho* compound passes with the steam into the distillate, the *para* compound remains behind.

***o*-Nitrophenol**

is a yellow crystalline solid, which melts at 45° . Its salts with alkali metals are deep red in colour.

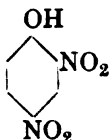
***p*-Nitrophenol**

is a white solid melting at 114° ; its alkali salts are bright yellow. Both of these compounds are more strongly acidic than unsubstituted phenols; this can be seen from the fact that sodium phenoxide C_6H_5ONa is decomposed by carbonic acid, whilst the sodium salts of the *o*- and *p*-nitrophenols are stable in presence of carbonic acid.

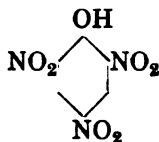
***m*-Nitrophenol**

is not formed by nitration of phenol, but can be prepared by an indirect method from *m*-dinitrobenzene. It is a white solid melting at 96° .

On further nitration of *o*- or *p*-nitrophenol, 2,4-dinitrophenol and ultimately 2,4,6-trinitrophenol are produced.

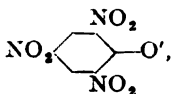
2.4-Dinitrophenol

is a pale yellow solid melting at 113° , which forms bright yellow salts. It is even more strongly acidic in character than the mono-nitrophenols, this increase in acidic character being due to the presence of the second nitro group in the molecule, for in 2.4.6-trinitrophenol we have an acid of strength approximating that of carboxylic acids.

2.4.6-Trinitrophenol or picric acid

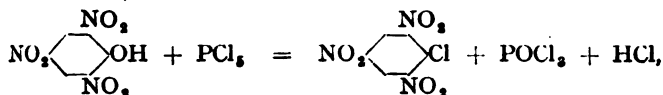
is usually prepared by gradually adding a solution of phenol in concentrated sulphuric acid to fuming nitric acid. It is a pale yellow crystalline solid, melting at 122° , which forms intensely yellow salts. It cannot be further nitrated.

The colour of picric acid in aqueous solution is more intense than in the solid state. This is due to the presence of the ion

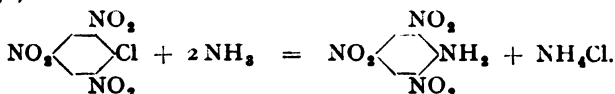


for in non-ionising solvents, as for instance paraffin hydrocarbons, picric acid is colourless. Addition of small quantities of alkalis to aqueous picric acid increases the colour, addition of strong mineral acids (by means of which the concentration of the picric ion is decreased, owing to the increase of total hydrogen ion concentration) diminishes the intensity of the colour. Thus picric acid forms a colourless solution in concentrated nitric acid.

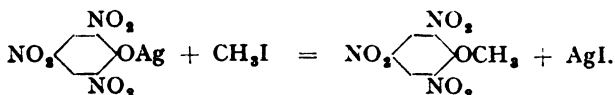
Not only is picric acid a strong acid in respect of ionic dissociation, but many of its derivatives behave like the corresponding derivatives of carboxylic acids. Thus on treatment with phosphorus pentachloride it yields *picryl chloride* (2.4.6-trinitrochlorobenzene) :



which is identical with the ultimate product of nitration of chlorobenzene. This substance behaves like a carboxylic chloride, yielding picric acid and hydrochloric acid on heating with water; and with ammonia the corresponding amino derivative, *picramide* (p. 371) :



On treating silver picrate with methyl iodide, 2,4,6-trinitro-anisole (methyl picrate) is formed :



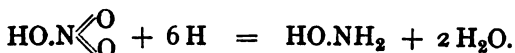
This is an ether, but behaves as an ester in being saponifiable by boiling with alkali. We thus see how the accumulation of nitro groups, which tend to exalt the acid properties of substances into which they are introduced, has converted a phenol into a substance closely resembling a true acid.

Picric acid possesses an intensely bitter taste, is poisonous, and decomposes explosively when detonated. The lead salt is a principal constituent of the explosive known as "Lyddite."

A peculiar property of picric acid is that of forming addition-products with many aromatic hydrocarbons, especially the more complicated of these (cf. naphthalene, p. 411). It also forms crystalline and sparingly soluble salts with many organic bases. It is occasionally employed as a dye for woollen fabrics.

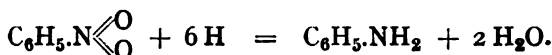
REDUCTION OF NITROBENZENE

When nitric acid is reduced by means of tin or zinc, it is converted into hydroxylamine :



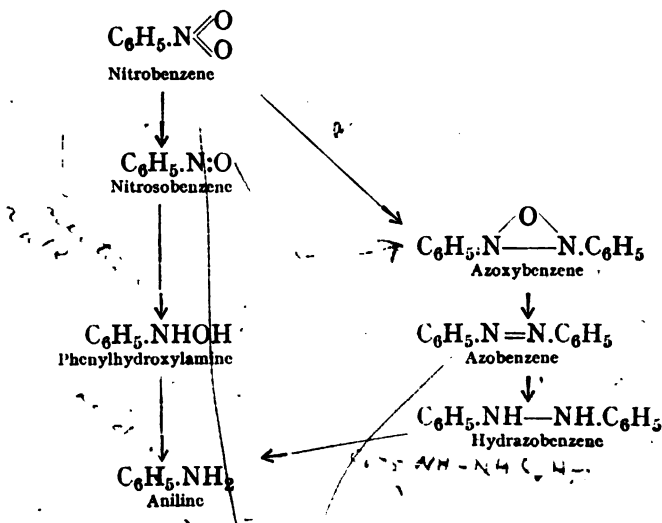
Similarly, nitrobenzene, on reduction in acid solution by reagents such as tin, zinc, iron, stannous chloride, etc., in presence

of hydrochloric acid, yields the corresponding amino derivative, amino benzene or *aniline* :

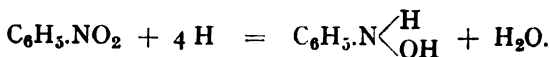


The properties of aniline and its derivatives we shall discuss in a later chapter.

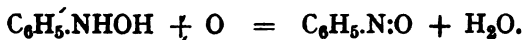
Between nitrobenzene and aniline a series of intermediate compounds is known. The formulæ and names of these are set forth in the following scheme, which shows their relation with one another :



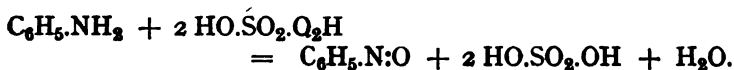
As above stated, reduction of nitrobenzene in acid solution leads to aniline. If, on the other hand, reduction be effected in neutral solution, as, for instance, by the action of zinc dust and water (or better, aqueous ammonium chloride, which dissolves zinc oxide), the reduction is arrested at an earlier stage, **phenylhydroxylamine** being formed :



This substance is undoubtedly an intermediate product both in the reduction of nitrobenzene to aniline and the oxidation of aniline to quinone (pp. 347, 362). On mild oxidation it yields **nitrosobenzene**:



which is also produced by the oxidation of aniline by means of persulphuric acid:



Both of these intermediate products, on reduction in acid solution, are converted into aniline.

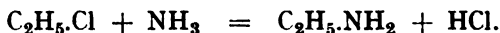
If nitrobenzene be treated with alkaline reducing agents, compounds containing two nitrogen atoms directly united are produced; an account of these will be given in a later chapter (p. 373).

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CHAPTER XXX

AROMATIC AMINO COMPOUNDS AND THEIR DERIVATIVES

AROMATIC amines bear to phenols the relation that aliphatic amines bear to alcohols. It has been pointed out that phenols, while partaking in the main of the general characteristics of the alcohols, nevertheless display many important minor differences. The same occurs in the amines; whilst aliphatic amines can be prepared by the action of ammonia upon alkyl halides:



An analogous reaction with aryl halides does not take place. Again, alkylamines are powerful bases, as strong as or stronger than ammonia; arylamines are also bases, but far weaker than ammonia.

The aryl radicle thus appears to be endowed with an acidic or negative tendency, exalting the acid character of the hydroxyl group in phenols, and depressing the basic character of the amino group in aromatic amines. This is borne out by the character of the di- and tri-arylamines; on successively replacing the hydrogen atoms in ammonia by aryl radicles, the basic character diminishes step by step, until with the tertiary amine it has vanished:

NH_3
Strong base

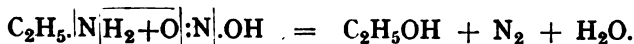
$\text{C}_6\text{H}_5\text{NH}_2$
Weak base

$(\text{C}_6\text{H}_5)_2\text{NH}$
Very weak base

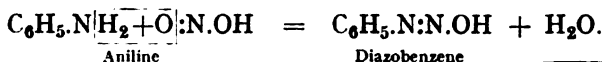
$(\text{C}_6\text{H}_5)_3\text{N}$
Neutral

This series forms a striking contrast with the series of methylamines, in which the basic character is increased by progressive replacement of the hydrogen atoms in ammonia by methyl groups.

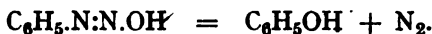
Other points of difference between aliphatic and aromatic amines will appear in the text. Chief of these is their behaviour towards nitrous acid. It will be recalled that aliphatic primary amines or their salts react in aqueous solution with nitrous acid, yielding the corresponding alcohol and elemental nitrogen :



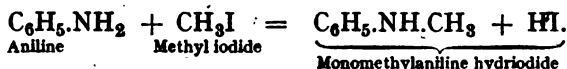
When an aromatic primary amine, on the other hand, is treated in the cold with nitrous acid, an intermediate product is formed, known as a *diazo* compound :



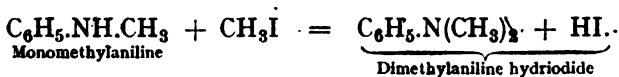
This is indubitably the most important reaction of aromatic primary amines : it will be discussed later in fuller detail. Suffice it here to remark that the analogy with the corresponding aliphatic compounds is completed by heating a solution of such a diazo compound, when elemental nitrogen is eliminated and a phenol is formed :



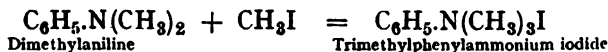
Aromatic primary amines, like the corresponding aliphatic compounds, react with alkyl halides, yielding salts of secondary amines :



these in turn react with more alkyl halide, yielding tertiary amines :

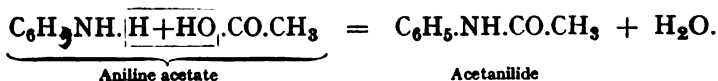


and these again can unite with alkyl halide to form quaternary salts :



Aromatic primary and secondary amines may be acylated ;

thus on warming with acetic anhydride or on boiling with acetic acid, acetyl derivatives are formed :

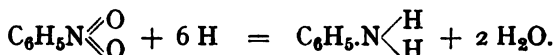


The amino group influences the aromatic nucleus in return for the effect of the nucleus in weakening the basicity of the amino group ; this is shown by the fact that the aryl portion of the molecule is rendered extremely susceptible to the action of substituting agents, such as halogens, and of oxidising agents.

Since the various aromatic amines differ but little from one another in chemical properties, the reactions of the simplest members of the series may be taken as typical of those of the remainder.

PRIMARY AMINES

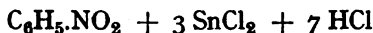
When nitrobenzene is treated with reducing agents, such as tin, zinc, or iron, with hydrochloric acid, or even with stannous chloride and hydrochloric acid, the two oxygen atoms of the nitro group (containing a quinquivalent nitrogen atom) are removed, and two atoms of hydrogen take their place, forming **aniline**, or *aminobenzene*, in which the amino group ($-\text{NH}_2$) contains a trivalent nitrogen atom :



Aniline is the simplest example of an aromatic primary amine, and is also the most important in industrial chemistry. Since it is readily obtainable from nitrobenzene, which in turn is easily produced by nitration of benzene, it is a far more accessible primary amine than any in the aliphatic series. It is produced on the manufacturing scale in an output of many tons daily, inasmuch as it forms the starting material for a large number of dyestuffs.

Aniline derives its name from the fact that it was first obtained by the distillation of indigo (in Spanish called " anil ") with strong caustic potash. It is now prepared exclusively from benzene, by nitration and reduction of the nitrobenzene

In the technical manufacture of aniline, the nitrobenzene is reduced by means of scrap iron and dilute hydrochloric acid at 90–100°; on completion of the reaction, an excess of lime is added, and the aniline thus liberated from its hydrochloride is driven over with steam. In laboratory practice it is usual to employ tin and hydrochloric acid, or stannous chloride alone :



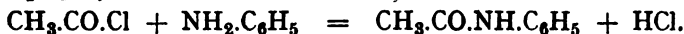
the mixture is then rendered alkaline with sodium hydroxide and distilled in a current of steam.

Aniline is a colourless liquid possessing a faint but characteristic odour. It boils at 183°, is volatile with steam, and is only slightly soluble in water. It is so weakly basic that it barely affects red litmus paper, but it is capable of forming stable salts with acids.

On treatment with acetic anhydride, acetyl chloride, or keten, and on boiling with acetic acid, acetanilide :

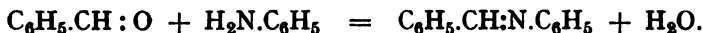


(cf. p. 368) is formed :

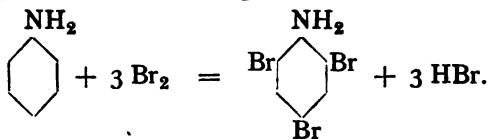


Other acyl radicles may be introduced in the same way.

Aniline condenses readily with aldehydes. With aliphatic aldehydes it yields more or less complex products; with aromatic aldehydes, such, for instance, as benzaldehyde (p. 384), it forms simple compounds called *anils*. Such an anil is *benzylideneaniline* (also called *benzalaniline*) :

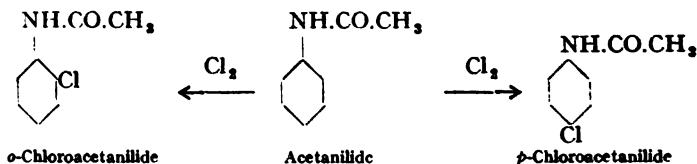


As already remarked, the nuclear hydrogen atoms in aniline may readily be substituted. Thus on treatment with bromine water, 2,4,6-*tribromoaniline* is produced :

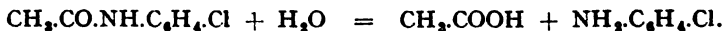


A sensitive and characteristic test for aniline is its behaviour on treatment in dilute aqueous solution with calcium hypochlorite or bleaching-powder, whereby an intense violet coloration is developed.

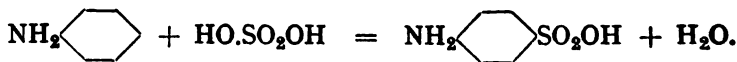
The chlorination or bromination of aniline, so as to produce monosubstitution-products, can be effected only indirectly, by converting the aniline into acetanilide and treating this with halogen, whereby *ortho* and *para* monochloro or monobromo-derivatives are formed :



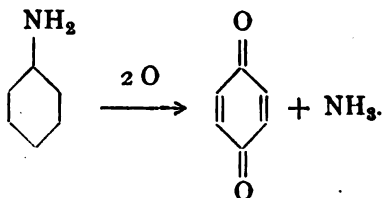
These derivatives of acetanilide, on hydrolysis by boiling with aqueous acids or alkalis, are converted into acetic acid and *o*-chloroaniline and *p*-chloroaniline respectively :



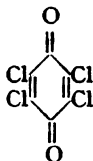
On heating aniline with sulphuric acid, sulphonation readily takes place, yielding aniline-*p*-sulphonic acid, or *sulphanilic acid* (p. 369) :



Aniline is easily oxidised, yielding quinone (p. 346) :

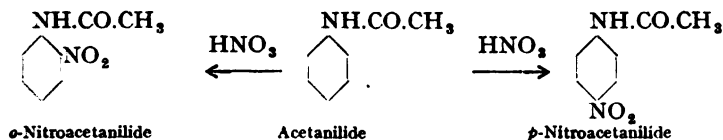


On treatment with potassium chlorate and concentrated hydrochloric acid, simultaneous oxidation and chlorination takes place, *chloroanil*, or tetrachloroquinone

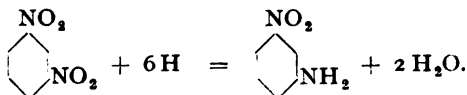


being formed.

Concentrated nitric acid vigorously attacks aniline, leading to tarry products; acetanilide, on the other hand, may be successfully nitrated, yielding a mixture of *ortho* and *para* **nitroacetanilides**:

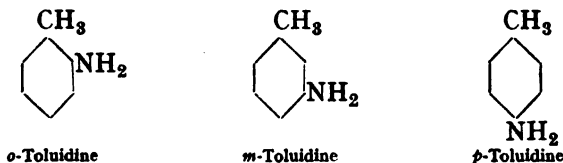


from which the corresponding *ortho* and *para* nitroanilines may be prepared by hydrolysis. The *meta* nitroaniline is not formed by this method; it is produced by partial reduction of *m*-dinitrobenzene (p. 351):



Before passing on to the consideration of the properties of such substituted derivatives of aniline, mention should be made of some of its homologues.

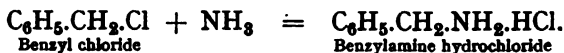
The three **toluidines**, or *aminotoluenes*:



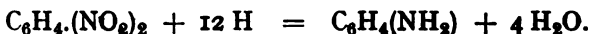
are compounds which closely resemble aniline in chemical behaviour. *Ortho* and *para* toluidines can be obtained directly from toluene, by nitration and subsequent reduction. *o*-Toluidine is a liquid which boils at 199° ; *p*-toluidine is a solid melting at 43° . *m*-Toluidine, a liquid boiling at 199° , can be prepared

only by an indirect method. The toluidines are of technical importance in forming the raw material for the manufacture of certain dyestuffs, of which the most prominent is *rosaniline* (p. 436).

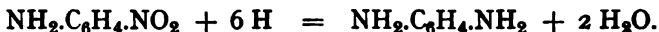
A fourth isomeric amino derivative of toluene is **benzylamine** $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, in which the amino group is attached to the extranuclear carbon atom. In character it is totally distinct from the toluidines, behaving strictly as an aliphatic primary amine. It is a strongly basic liquid, miscible in all proportions with water. It boils at 183° . It is formed by the action of ammonia upon benzyl chloride :



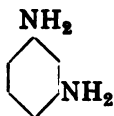
DIAMINES.—When a dinitro compound is vigorously reduced, as with tin and hydrochloric acid, both nitro groups are converted into amino groups. Thus each of the three isomeric dinitrobenzenes on reduction yields the corresponding **phenylenediamine** or *diaminobenzene* :



They may also be produced by reduction of the corresponding nitro derivative of amines, such as the nitroanilines (see below) :



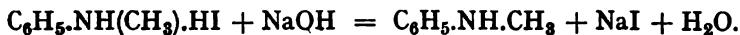
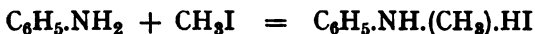
Aromatic diamines are colourless solids, more soluble in water and more strongly basic than aromatic monoamines. The most important is *m*-phenylenediamine :



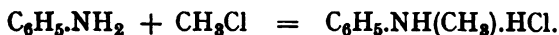
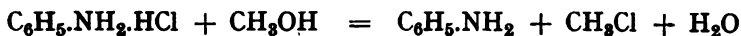
prepared by reduction of *m*-dinitrobenzene. It is employed in the manufacture of certain dyestuffs. The *ortho* and *para* isomers may be most conveniently obtained by reducing the corresponding nitroanilines.

SECONDARY AMINES

Aniline and its homologues, like aliphatic primary amines, yield secondary amines on treatment with alkyl iodides. Thus aniline, on treatment with methyl iodide, yields **monomethylaniline** :



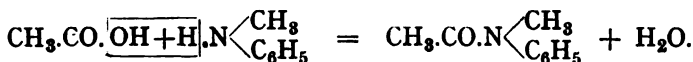
Monomethylaniline is a liquid which closely resembles aniline. It boils at 193° . It is technically prepared by heating aniline hydrochloride with methyl alcohol; in this reaction it is assumed that methyl chloride is formed as an intermediate product :



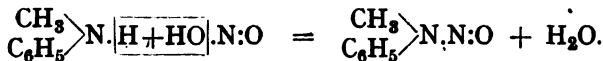
In its chief properties it is a typical secondary amine; on treatment with an alkyl halide it yields a tertiary amine :



like aniline it readily yields acyl derivatives, such as *acetyl methylaniline* (or *methylacetanilide*) :



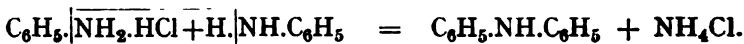
With nitrous acid, the hydrogen atom attached to nitrogen is replaced by a nitroso ($-\text{N}:\text{O}$) group, yielding a *nitrosoamine* :



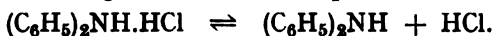
It will thus be seen that in general chemical behaviour the mixed aliphatic aromatic secondary amines—of which methylaniline is typical—closely resemble the purely aliphatic secondary amines.

Of the purely aromatic secondary amines the most important member is **diphenylamine** $\text{C}_6\text{H}_5.\text{NH}.\text{C}_6\text{H}_5$. This is a colourless crystalline solid, melting at 54° , boiling at 310° . It is prepared

by heating aniline hydrochloride with aniline, whereby ammonium chloride is eliminated :

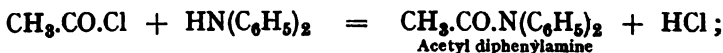


As already remarked, diphenylamine is a weaker base than aniline. It is capable of forming salts, such as the hydrochloride $(\text{C}_6\text{H}_5)_2\text{NH}.\text{HCl}$, but these are decomposed (hydrolysed) by water, according to the balanced equation :

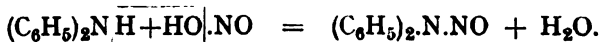


Salts of aniline are not hydrolysed in this way.

Diphenylamine is employed in analytical chemistry for the detection of traces of nitric and nitrous acids, which develop with it in presence of strong sulphuric acid an intense blue coloration. On treatment with acetic anhydride or acetyl chloride, it yields the acetyl derivative :

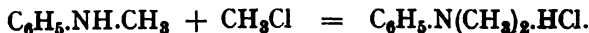
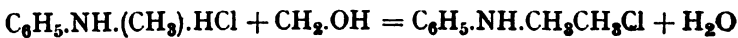


with nitrous acid, under suitable conditions, it yields *diphenyl-nitrosoamine* :



TERTIARY AMINES

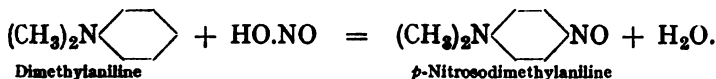
When aniline hydrochloride is heated with methyl alcohol, the first reaction consists in the formation of the hydrochloride of monomethylaniline (p. 365). If an excess of methyl alcohol be present, the second hydrogen atom of the amino group is replaced by a methyl radicle, yielding the hydrochloride of dimethylaniline :



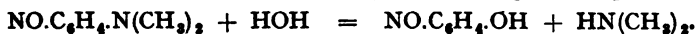
Dimethylaniline $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ is a colourless liquid of characteristic odour. It solidifies at 0° and boils at 193° . Like the partly aliphatic tertiary amines, dimethylaniline unites with alkyl halides to form quaternary ammonium salts (p. 200).

It also resembles the aliphatic tertiary amines in its inability to react with acetylating reagents, such as acetic anhydride.

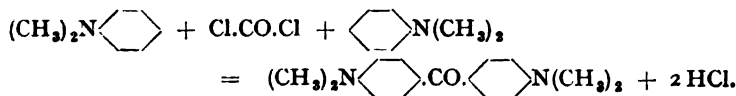
On the other hand, it is capable of reacting with nitrous acid, whereas it will be recalled that aliphatic tertiary amines are unchanged by this reagent. In dimethylaniline, the presence of the dimethylamino [$-\text{N}(\text{CH}_3)_2$] group has so influenced the character of the phenyl radicle that the *para* hydrogen atom is readily displaceable by other groups. Thus with nitrous acid (by adding sodium nitrite to an aqueous solution of a salt of dimethylaniline) the *para* nitroso derivative is at once produced :



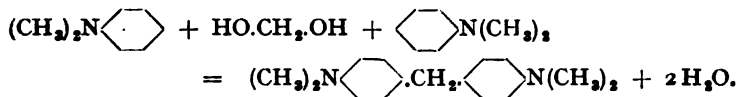
p-Nitrosodimethylaniline is a green crystalline solid, which possesses weakly basic properties. It is hydrolysed on boiling with alcoholic potash, breaking down into dimethylamine and *p*-nitrosophenol :



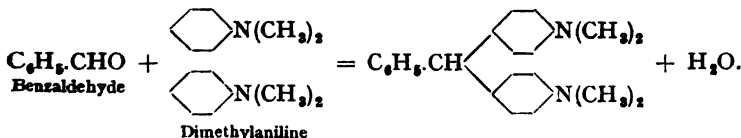
Dimethylaniline also reacts with carbonyl chloride COCl_2 , yielding a derivative of benzophenone (p. 390) called *Michler's ketone*, or, more strictly, *p,p*-tetramethyldiaminobenzophenone :



It also condenses with formaldehyde, in presence of aqueous hydrochloric acid, to a derivative of diphenylmethane (p. 325), *p,p*-tetramethyldiaminodiphenylmethane :

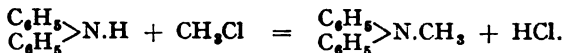


With benzaldehyde (p. 383) in the presence of hydrogen chloride, an analogous compound is formed, a derivative of triphenylmethane (p. 325) :



This product, on oxidation in presence of hydrochloric acid, yields a green dyestuff called "malachite green" (p. 437).

Methyl diphenylamine (C_6H_5)₂.N.CH₃ is prepared by heating diphenylamine with methyl alcohol and hydrochloric acid. The reaction follows the same course as the methylation of aniline :



It is a weakly basic liquid, boiling at 292°.

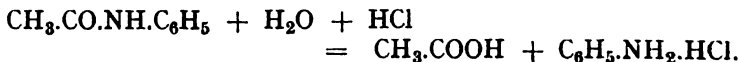
Triphenylamine (C_6H_5)₃N may be prepared by heating iodobenzene with diphenylamine in presence of a mixture of copper powder, cuprous iodide, and potassium carbonate. It is a neutral substance, entirely incapable of forming a salt even with dry hydrogen chloride. It melts at 127°.

ACYL DERIVATIVES OF AROMATIC AMINES

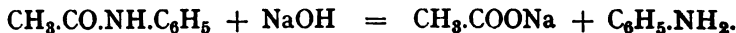
Typical of these is **acetanilide** $\text{CH}_3\text{CO.NH.C}_6\text{H}_5$, the modes of formation of which have been mentioned on p. 361. It is a colourless crystalline solid, melting at 115°, boiling at 304°.

It may be regarded as acetamide in which a phenyl radicle replaces one of the amidic hydrogen atoms. It bears out this relation in its capability of being hydrolysed by treatment with acid or alkaline hydrolytic reagents.

On prolonged boiling with aqueous mineral acid it yields acetic acid and a salt of aniline :



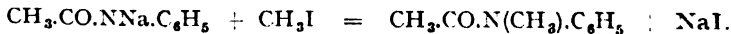
with alkalis it yields free aniline and an acetate :



Owing to the negative character of the phenyl group, acetanilide possesses certain slightly acidic properties. On treatment with sodium, hydrogen is evolved, and a sodium salt is produced :



This salt reacts with alkyl halides, yielding the acetyl derivative of a secondary amine; thus with methyl iodide, **acetylmethylaniline** (or **methylacetanilide**, p. 365) is produced :

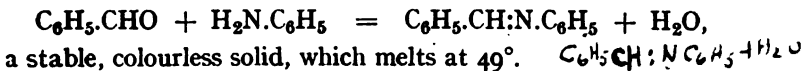


This compound, on hydrolysis, yields acetic acid and methylaniline. This formed at one time a technical method for the preparation of methylaniline.

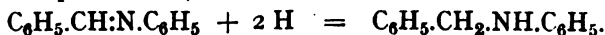
Acetanilide possesses valuable physiological properties; it has been largely employed as an antipyretic under the name "Anti-febrin."



The condensation between benzaldehyde (p. 385) and aniline takes place with extreme readiness—the two substances at once react when warmed together, alone or in alcoholic solution—yielding **benzylideneaniline** (or **benzalaniline**):

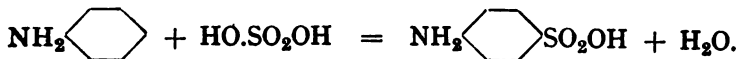


On reduction it is converted into the secondary amine **benzylaniline** (which can also be formed by the action of benzyl chloride upon aniline):

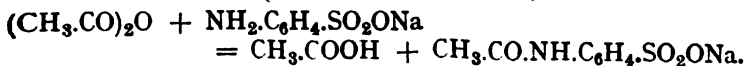


AMINO SULPHONIC ACIDS

Sulphanilic acid is the name given to the compound formed by heating aniline with sulphuric acid—*aniline-p-sulphonic acid*:



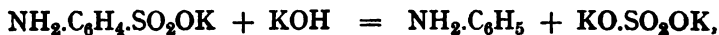
Sulphonation takes place more readily with aniline than with benzene, owing to the influence of the amino group upon the phenyl radicle. Since the molecule contains both a basic radicle (—NH_2) and an acidic radicle ($\text{—SO}_2\text{OH}$), these groups affect each other, diminishing the acidic character of the sulphoxyl group and entirely destroying the salt-forming properties of the amino group. The sodium salt of sulphanilic acid, on the other hand, is a base. Thus sulphanilic acid itself cannot be acetylated; the sodium salt, however, yields an acetyl derivative on boiling with acetic anhydride:



It is therefore probable that sulphanilic acid exists as an internal salt such as



It is a white solid, containing water of crystallisation, which does not melt, but carbonises on heating above 280° . It differs from the majority of sulphonic acids in its behaviour on fusion with potassium hydroxide, yielding aniline and potassium sulphate :



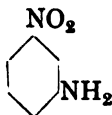
instead of the aminophenol and potassium sulphite which might have been expected.

NITROANILINES

Dinitrobenzenes may be partially reduced by passing the necessary amount of hydrogen sulphide into an ammoniacal alcoholic solution. The ammonium sulphide thus formed reduces one of the nitro groups to an amino group, yielding a nitroaniline :

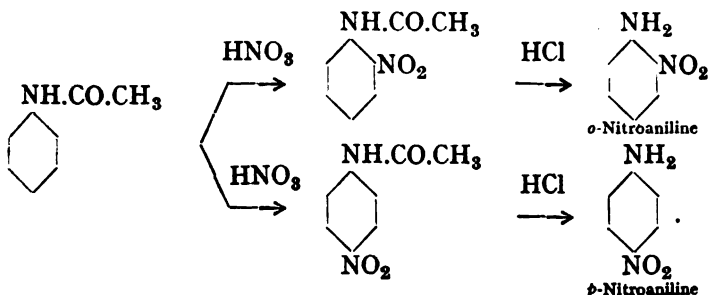


m-Nitroaniline

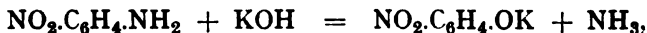


thus prepared from m-dinitrobenzene (p. 351) is a crystalline solid of brilliant yellow colour, melting at 114° . It possesses basic properties, and forms salts which are stable in presence of water.

The *ortho* and *para* nitroanilines can also be prepared by partial reduction of the corresponding dinitrobenzenes ; as, however, these latter are not obtainable by direct nitration of benzene, the most convenient method of preparation consists in nitrating acetanilide (p. 368), and hydrolysing the resulting nitroacetanilides by boiling with aqueous mineral acid :



These compounds are yellow solids. They are considerably weaker bases than *m*-nitroaniline, and are, unlike the latter, decomposed by boiling with concentrated alkali, yielding ammonia and a salt of the corresponding nitrophenol :



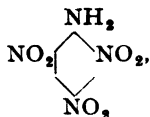
thereby resembling the carboxylic amides in their behaviour towards alkali. The acetyl derivatives of these nitroanilines are so strongly acid that they dissolve in cold aqueous potassium hydroxide :



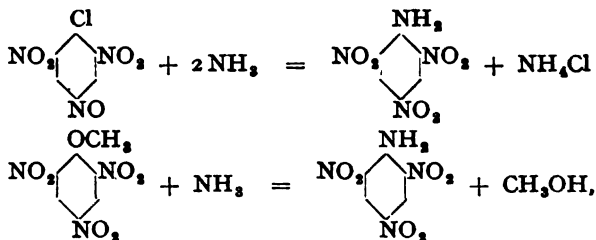
The *meta* isomer, like acetanilide itself, is insoluble in cold alkali.

This phenomenon—that the negative effect of the nitro group is most appreciable when situated in the *ortho* or *para* positions—is notable, especially when considered in connection with the fact that the nitro group possesses the *meta* directing influence (p. 315). The rationale of this relation has not yet been fully elucidated ; at present we cannot do more than direct attention to its existence.

In 2.4.6.*trinitroaniline*, or *pleramide*,

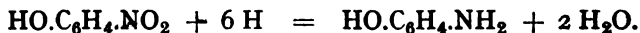


this effect is even more marked, owing to the accumulation of nitro groups situated in positions *ortho* and *para* to the amino group. This compound behaves in every way like a carboxylic amide, and is in fact produced, like such amides, by the action of ammonia upon not only the chloride of picric acid, 2.4.6.trinitrochlorobenzene (p. 355), but upon 2.4.6-trinitroanisole (methyl picrate) :



reactions recalling the formation of amides by the action of ammonia upon carboxylic chlorides and esters (pp. 170, 173).

AMINOPHENOLS are prepared by the reduction of nitrophenols (p. 353) :



In these compounds the acid character of the phenolic hydroxyl group has disappeared ; they are, on the other hand, capable of forming salts with acids. They are very soluble in water, and are readily oxidised. **p-Aminophenol**



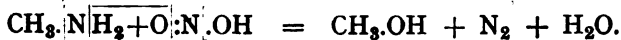
is for this reason often employed as a constituent of photographic developers (p. 345). On oxidation with chromic acid it yields quinone (p. 347).

CHAPTER XXXI

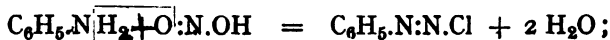
AROMATIC COMPOUNDS CONTAINING NITROGEN ATOMS DIRECTLY UNITED

DIAZO COMPOUNDS AND THEIR REACTIONS

WHEN an aliphatic primary amine or one of its salts is treated with nitrous acid, an immediate reaction ensues, whereby nitrogen is evolved and a hydroxyl group takes the place of the amino group (p. 340) :



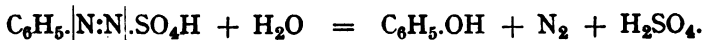
When, however, a salt of an aromatic primary amine is treated with nitrous acid, the reaction proceeds in two stages. The first stage consists in the elimination of water :



Aniline hydrochloride

Diazobenzene chloride

the intermediate product is termed a **diazo** compound. If an aqueous solution containing a diazo compound—such as is produced by the action of nitrous acid upon a solution of aniline or one of its salts—be heated, the second stage of the reaction is brought about ; a phenol is formed with elimination of elemental nitrogen :



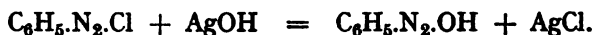
Diazobenzene sulphate

Phenol

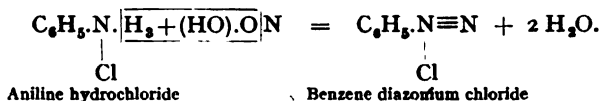
It will be seen that the net result of these two reactions is, as in the case of the aliphatic amines, replacement of an amino group by a hydroxyl group. It is probable that the reaction

with aliphatic amines an unstable diazo compound is at first produced, but at once decomposes in the sense of the second stage. The peculiar nature of the aromatic nucleus renders the intermediate product more stable in the case of aniline and allied compounds.

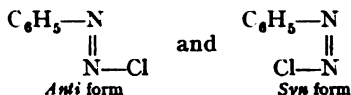
Diazo compounds are salts of strong bases, resembling quaternary ammonium compounds in existing always in a combined state with hydroxyl or acidic groups. Diazo hydroxides may be prepared by the same method as quaternary ammonium hydroxides—by treatment of an aqueous solution of a halide with silver oxide:



For this and other reasons these salts have been formulated by some authorities as derivatives of quinquevalent nitrogen, and are called *diazonium salts*:



It has also been found that diazo compounds exist in isomeric forms, to which the alternative formulæ, such as $\text{C}_6\text{H}_5\text{.N:N.Cl}$, are more suitably assigned. Furthermore there is evidence that such diazo compounds can exist in two stereoisomeric forms, expressible by:



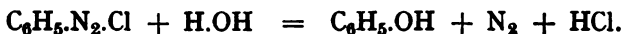
analogous to the maleic and fumaric type of isomerism (cf. p. 269). The question is still unsettled, so we shall content ourselves by representing diazo compounds by the mode of formulation $\text{C}_6\text{H}_5\text{.N}_2\text{.Cl}$.

Diazo compounds in general are unstable substances, often explosively so in the dry state, but are not explosive in aqueous solution. On account of their wide scope of reactions they are of great importance both in synthetic and in industrial chemistry.

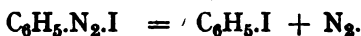
The most convenient method of preparation is to add to an ice-cold solution of the amine in dilute mineral acid the requisite quantity of sodium nitrite. This is known as *diazotisation*. It is rarely necessary to isolate diazo compounds, since their

aqueous solutions are as a rule suitable for subsequent reactions ; in a few cases, however, it is convenient to diazotise in alcoholic solution.

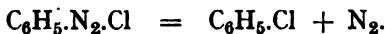
As above stated, a solution of a diazo salt, such as a chloride or sulphate, yields nitrogen and a phenol on heating :



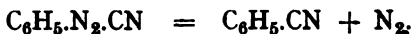
If potassium iodide be added to such a solution, which is thereupon heated, a different reaction takes place, yielding an iodo compound and nitrogen :



This reaction takes place even more readily in the presence of cuprous iodide ; and diazo chlorides and bromides, which yield phenol when heated in aqueous solution alone, are in the presence of the corresponding cuprous halide and halogen hydracid converted into the chloro and bromo compounds :

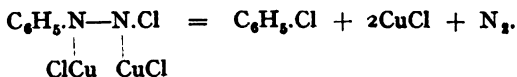


A similar reaction occurs when a diazo salt, such as the chloride, is heated with a solution of cuprous cyanide and potassium cyanide, cyano compounds (nitriles, p. 394) being formed :

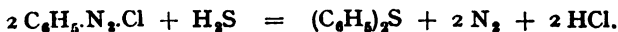


This decomposition of diazo compounds in presence of cuprous salts is known as **Sandmeyer's reaction**.

The cuprous halide in each case forms an unstable addition-product with the diazo compound, which breaks down on heating, regenerating the cuprous salt—probably in the sense of the equation :

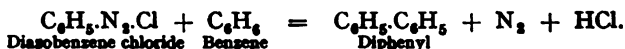


Other radicles may also be introduced by suitable treatment of diazo compounds ; thus, with hydrogen sulphide, diphenyl sulphide (p. 336) is formed :



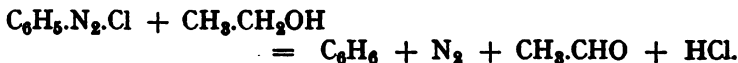
In presence of excess of hydrogen sulphide, thiophenol (p. 335) $\text{C}_6\text{H}_5\cdot\text{SH}$ is the chief product.

Even aromatic radicles can be introduced by warming a dry diazo compound with excess of an aromatic hydrocarbon :

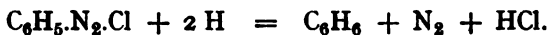


This last reaction often proceeds more readily in the presence of a small quantity of aluminium chloride.

If a diazo compound be boiled with alcohol, reduction takes place with formation of the corresponding hydrocarbon, the alcohol being oxidised to aldehyde :

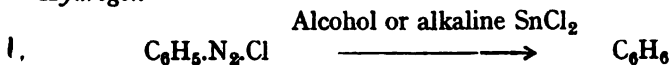


The same reduction is effected in aqueous solution by treatment with alkaline stannous chloride :

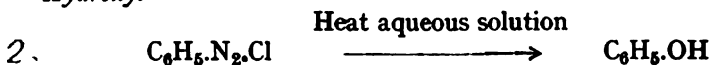


From the foregoing it can be seen how numerous are the atoms or radicles by which the amino group in aromatic primary amines can be replaced by the aid of the diazo reaction. The more important of these conversions are here recapitulated :

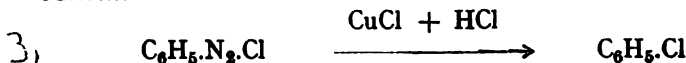
Hydrogen—



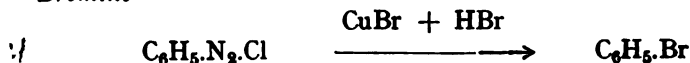
Hydroxyl—



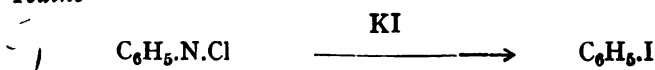
Chlorine—



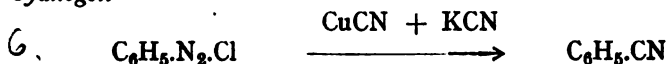
Bromine—



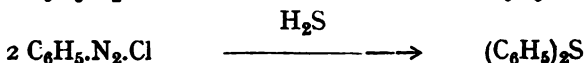
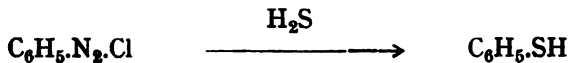
Iodine—



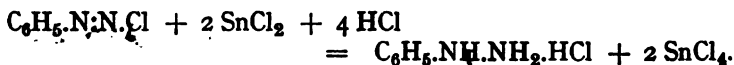
Cyanogen—



Sulphur—



If diazobenzene chloride be reduced with stannous chloride in acid solution, nitrogen is not eliminated, but the diazo grouping takes up four atoms of hydrogen, yielding the hydrochloride of a new base, *phenylhydrazine* :

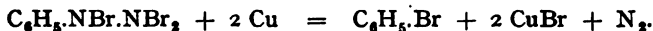


The properties of this important compound will be discussed below.

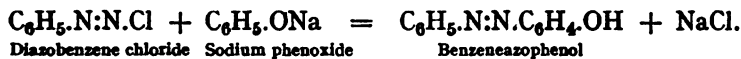
Just as diazobenzene salts are capable of combining with hydrogen, so can they unite with bromine in presence of potassium bromide, forming *diazobenzene perbromide* :



On treating diazobenzene perbromide with finely powdered metallic copper, part of the bromine is eliminated as cuprous bromide, nitrogen is evolved, and bromobenzene is formed :



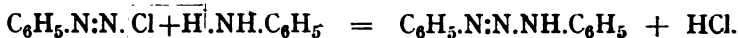
A characteristic and important reaction of diazo compounds is that of "coupling" with phenols in alkaline solution, *azo* compounds (see below) being produced :



The hydroxylated azo compounds thus formed are coloured substances ; hence this reaction is largely employed in the manufacture of dyestuffs.

On treatment of a diazobenzene salt with aniline, a different

type of reaction takes place: one of the hydrogen atoms attached to the nitrogen atom in the aniline is replaced, leading to *diazoaminobenzene*:

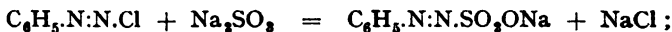


This product will again be referred to below (p. 382).

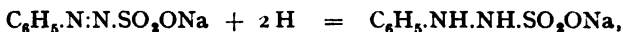
PHENYLHYDRAZINE

It has just been stated that when diazobenzene chloride is treated with a solution of stannous chloride in hydrochloric acid, it is reduced to phenylhydrazine $\text{C}_6\text{H}_5\text{.NH.NH}_2$.

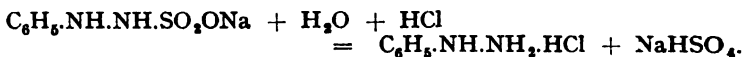
An alternative method of preparation, which is in fact the technical method for its production on a large scale, is the following: diazobenzene chloride interacts in aqueous solution with sodium sulphite, yielding *sodium benzenediazosulphonate*:



this solution is then treated with zinc dust and acetic acid, whereby *sodium phenylhydrazinesulphonate* is formed:

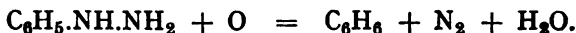


which undergoes hydrolysis on boiling with hydrochloric acid, yielding phenylhydrazine hydrochloride:

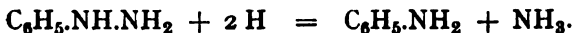


Phenylhydrazine is a colourless basic substance, sparingly soluble in water, which melts at 17° and boils at 241° . It is of especial interest on account of its faculty for forming condensation-products with aldehydes and ketones.

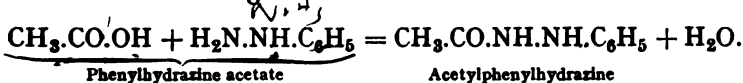
With mild oxidizing agents, such as Fehling's solution or other cupric salts, phenylhydrazine is readily oxidised, yielding benzene, nitrogen and water:



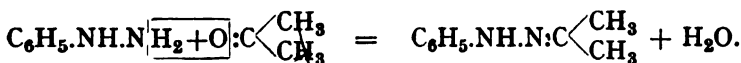
With powerful reducing agents, such as zinc in presence of hydrochloric acid, the linkage between the nitrogen atoms is broken, aniline and ammonia being formed:



Phenylhydrazine resembles aniline in yielding an acetyl derivative on heating with acetic acid :

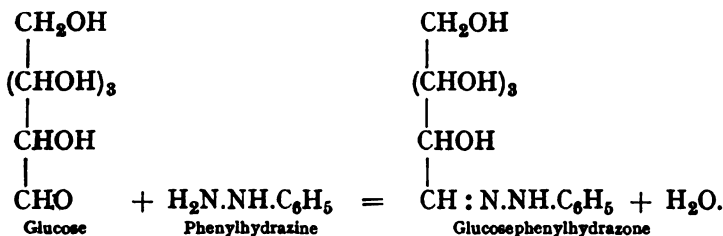


On warming phenylhydrazine or its acetate with an aldehyde or a ketone, water is eliminated with formation of a *phenylhydrazone* (cf. p. 144) :



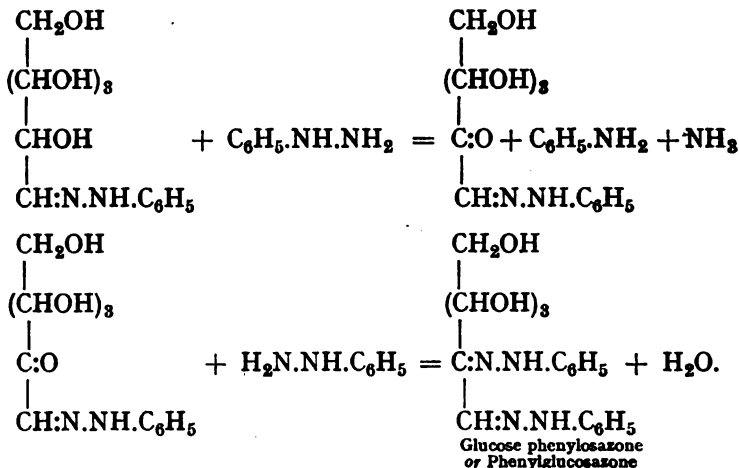
This reaction takes place with such extreme readiness that it can be brought about with phenylhydrazine acetate even in dilute aqueous solution. The phenylhydrazones so formed are important derivatives of carbonyl compounds, and are employed for the identification of aldehydes and ketones.

Phenylhydrazine finds an important field in its application to the chemistry of the sugars (p. 273). When a solution of a sugar, such as glucose, is warmed with phenylhydrazine acetate, a yellow insoluble precipitate, called an *osazone*, is formed. This reaction takes place in several stages: the first stage is the formation of a phenylhydrazone in the ordinary way :



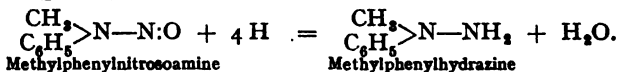
The glucosephenylhydrazone, which is soluble in water, acts towards the phenylhydrazine as a reducing agent, yielding aniline and ammonia, and is itself converted into an intermediate carbonyl compound, which at once combines

with a further quantity of phenylhydrazine, yielding an *osazone* :



The osazones so formed are characteristic derivatives of the different sugars.

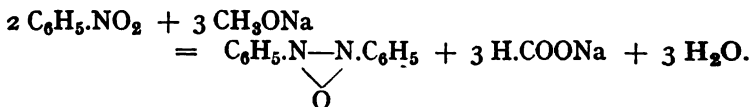
Secondary hydrazines are produced by the reduction of nitrosoamines (p. 365) :



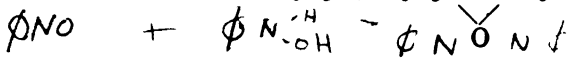
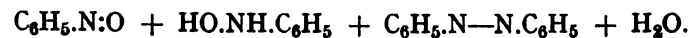
They resemble primary hydrazines (exemplified by phenylhydrazine) in many of their chemical properties.

AZOXYBENZENE

When nitrobenzene is boiled with a solution of sodium methoxide in methyl alcohol, reduction of the nitrobenzene takes place, the methoxide being converted into formate ; the nitrobenzene is not completely reduced to aniline, but two molecules unite, yielding a yellow crystalline solid called **azoxybenzene** :

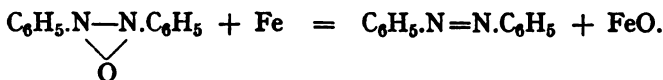


This substance is also produced by the action of nitrosobenzene (p. 357) upon phenylhydroxylamine (p. 356) :

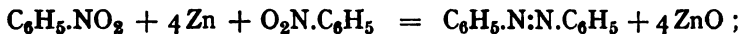


AZOBENZENE

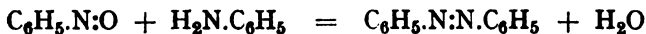
Azoxybenzene may be reduced by distilling it with iron filings, when azobenzene results :



Azobenzene can also be produced directly from nitrobenzene by reduction in alcoholic solution in presence of alkali by means of zinc dust, sodium amalgam, or an alkaline solution of stannous chloride :

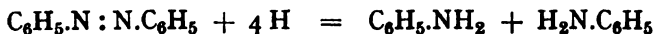


likewise by the interaction of nitrosobenzene and aniline :



Azobenzene is a red crystalline substance, which melts at 68° and boils at 295° . It is extremely stable ; we see here the effect of the phenyl radicle in increasing the stability of compounds containing the grouping —N=N— . Aliphatic diazo compounds are not formed at all by the action of nitrous acid upon aliphatic primary amines ; aromatic diazo compounds, as we have just seen, are decomposed by heating their aqueous solutions ; whilst azobenzene, in which two phenyl radicles are present in the molecule, is so stable that it can be heated to its boiling-point without decomposition.

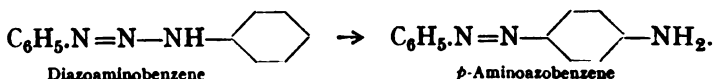
On vigorous reduction, as by means of tin or stannous chloride with hydrochloric acid, azobenzene is converted into aniline, by rupture of the linkage between the nitrogen atoms :



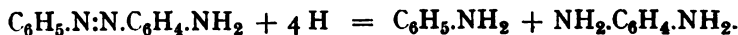
Azobenzene is the parent substance of a large number of dye-stuffs (p. 430). Though coloured, it is itself not a dyestuff, since

it does not possess the property of "fixing" itself upon fibres of wool, cotton, or silk.

An important derivative of azobenzene is *p*-aminoazobenzene. This is produced by the action of diazobenzene chloride upon aniline; in technical practice it is customary to prepare it by adding one molecular proportion of sodium nitrite to a solution of two molecular proportions of aniline hydrochloride. When diazoaminobenzene is treated with hydrochloric acid, one of the nitrogen atoms shifts into the position in the nucleus *para* to that which it originally occupied, leading to the *para* amino derivative of azobenzene:

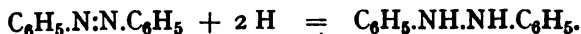


A similar intramolecular rearrangement takes place with *hydrazobenzene*, an account of which will be given below. *p*-Aminoazobenzene is an intensely yellow substance, and is a true dyestuff. It possesses weak basic properties, and yields stable salts; the hydrochloride is employed in the dyeing industry under the name "aniline yellow." On reduction with tin and hydrochloric acid it yields a mixture of aniline and *p*-phenylenediamine:



HYDRAZOBENZENE

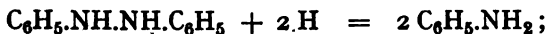
It has just been stated that azobenzene, on vigorous reduction in acid solution, is broken down into two molecules of aniline; on reduction in alkaline solution, the molecule is not torn asunder, but two atoms of hydrogen are taken up. Thus on treating azobenzene in alcoholic solution with zinc and alkali or with alcoholic ammonium sulphide, *hydrazobenzene* is produced:



This is a colourless crystalline substance, which is readily reoxidised to azobenzene. Although it is a derivative of hydrazine, it

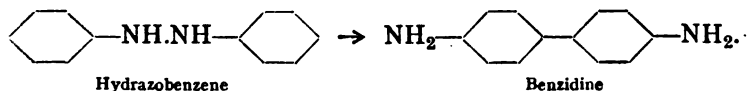
does not undergo the same general reactions as phenylhydrazine, owing to the absence of an unsubstituted amino group. In this respect it differs from the isomeric substance *diphenylhydrazine* (C_6H_5)₂N.NH₂, formed by the reduction of diphenylnitrosoamine (p. 366), which reacts with aldehydes and ketones to form diphenylhydrazones such as $(C_6H_5)_2N.N:CH.CH_3$.

On reduction with tin or stannous chloride and hydrochloric acid, hydrazobenzene, like azobenzene, yields aniline :

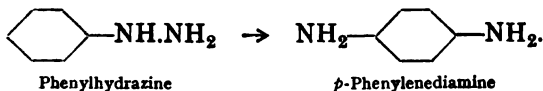


in this behaviour also resembling phenylhydrazine, which yields aniline and ammonia on reduction (p. 379).

The most striking reaction which hydrazobenzene undergoes is an intramolecular change. On warming with concentrated hydrochloric acid, both nitrogen atoms wander to the *para* positions of the phenyl radicles to which they were originally attached, yielding the di-*para* amino derivative of diphenyl (p. 325), known as *benzidine*:



A similar intramolecular transformation is shown by phenylhydrazine itself, which can be converted into *p*-phenylenediamine :



Both of these isomeric changes are closely akin to the conversion of diazoaminobenzene into aminoazobenzene (p. 382).

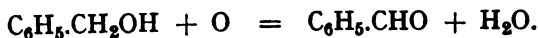
Benzidine behaves in every way as an aromatic primary amine. It is of considerable technical importance, since many valuable azo dyestuffs can be prepared from it by means of the diazo reaction.

CHAPTER XXXII

AROMATIC ALDEHYDES AND KETONES

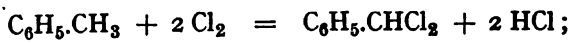
AROMATIC ALDEHYDES resemble the corresponding compounds in the aliphatic series in their general properties, the chief points of difference being those due to the presence in the molecule of an aromatic radicle.

The most important of the aromatic aldehydes is **benzaldehyde** $C_6H_5.CHO$. This is the aldehyde corresponding to benzyl alcohol (p. 342), and may be prepared from it by oxidation in acid solution :

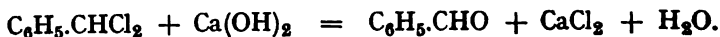


It is a colourless liquid which boils at 180° . Its odour is characteristic, being that associated with bitter almonds, from which it was first obtained ; for this reason benzaldehyde is occasionally called " oil of bitter almonds."

Synthetically it may be prepared in a variety of ways. In technical practice it is produced from toluene ; this is treated at its boiling-point with chlorine, so as to produce benzylidene chloride (benzal chloride, p. 331) :



the benzal chloride is thereupon heated with a mixture of water and calcium hydroxide, whereby it is converted into benzaldehyde :

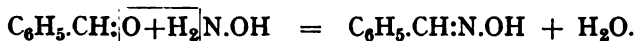


It is also formed by the action of chromyl chloride CrO_2Cl_2

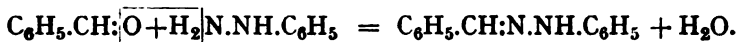
upon toluene, and by heating a dry mixture of calcium benzoate and calcium formate :



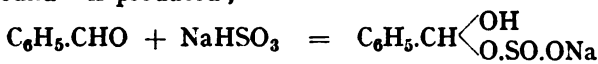
Benzaldehyde can undergo almost all the reactions typical of aldehydes ; it yields an oxime (*benzaldoxime*) with hydroxylamine :



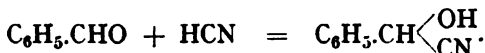
With phenylhydrazine it forms *benzaldehydephenylhydrazone* :



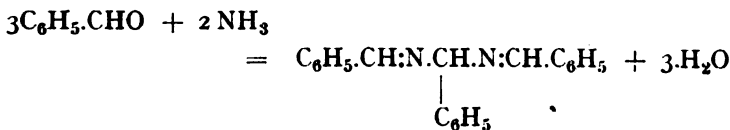
with sodium hydrogen sulphite a crystalline "bisulphite compound" is produced ;



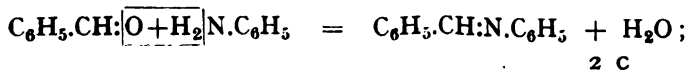
and with hydrogen cyanide it forms *benzaldehyde cyanohydrin*, also called *mandelonitrile* :



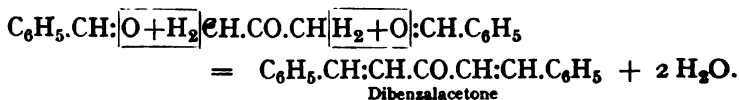
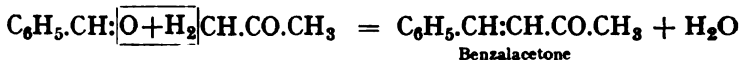
Its behaviour towards ammonia, however, differs from that of the majority of aldehydes, since no aldehyde-ammonia is formed. The reaction which takes place resembles rather the formation of hexamethylenetetramine (p. 148) from formaldehyde and ammonia, for a compound free of oxygen, called *hydrobenzamide*, is produced :



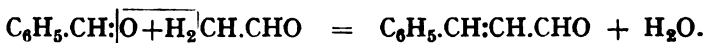
Benzaldehyde readily forms condensation-products with other compounds by elimination of water ; thus with aniline it yields *benzal-* (or *benzylidene-*) *aniline* :



and with aqueous acetone in the presence of a small quantity of alkali it yields *benzalacetone* and *dibenzalacetone* :



By the action of a trace of alkali upon a mixture of benzaldehyde and acetaldehyde, *cinnamic aldehyde*, the odorous constituent of cinnamon, is produced :



Benzaldehyde may, like the aliphatic aldehydes, be reduced to the corresponding alcohol :



Oxidation is not brought about so readily as in the aliphatic series, but may be effected by alkaline permanganate, yielding benzoic acid :

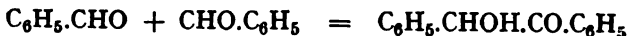


The action of alcoholic potassium hydroxide is interesting, since it does not, as in the case of the majority of aliphatic aldehydes, lead to the formation of aldehyde resins, but converts benzaldehyde into equimolecular quantities of benzyl alcohol and potassium benzoate :

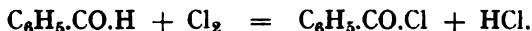


a reaction recalling the exceptional behaviour of formaldehyde, which yields methyl alcohol and a formate on heating with concentrated alkali (p. 148).

A singular reaction takes place on boiling benzaldehyde with a concentrated solution of potassium cyanide ; two molecules unite together to form the ketonic alcohol *benzoin* :

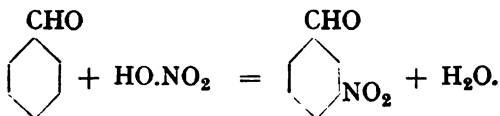


On treatment with dry chlorine, benzaldehyde is converted into *benzoyl chloride*, the chloride of benzoic acid (p. 391) :

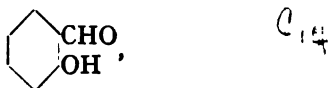


Bromine reacts similarly.

Nitric acid does not oxidise benzaldehyde to benzoic acid, but nitrates it, yielding *m-nitrobenzaldehyde* :



Of the other substituted derivatives of benzaldehyde, one of the most important is **salicylaldehyde** (*o-hydroxybenzaldehyde*),

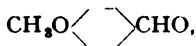


which occurs in certain plants. Synthetically it is prepared by heating chloroform with an alkaline solution of phenol :



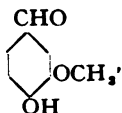
This is known as *Reimer's reaction* ; it leads to the simultaneous production of both *ortho* and *para* hydroxybenzaldehydes, which are separated by acidifying the reaction-mixture and distilling with steam, whereby the volatile *ortho* compound passes over with the steam, leaving the *para* derivative behind.

Anisaldehyde (*p-methoxybenzaldehyde*),

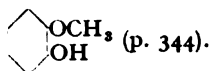


produced by the oxidation of *anethole* $\text{CH}_3\text{O.C}_6\text{H}_4\text{CH:CH.CH}_3$ (the odorous principle of aniseed oil), is a liquid which boils at 245° . It is employed in the manufacture of artificial perfumes.

Vanillin,



the odorous principle of vanilla, is produced by Reimer's reaction from guaiacol,

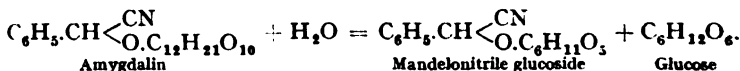


It was above stated that benzaldehyde was first obtained from bitter almonds. Bitter almonds contain a substance known as *amygdalin*, which, on boiling with dilute acids, yields benzaldehyde, hydrogen cyanide, and glucose. This same decomposition is brought about by a hydrolytic enzyme, called *emulsin*, which is present in the skin of the almonds, so that when the whole almond is crushed in presence of a little water, the odours of benzaldehyde and hydrogen cyanide can be observed.

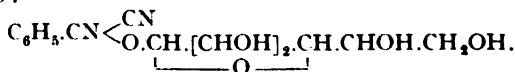
Amygdalin belongs to the family of glucosides; it is a compound formed between benzaldehyde cyanohydrin and two molecules of glucose :



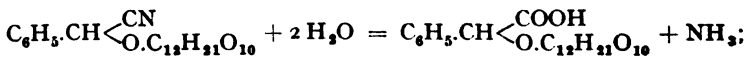
The two glucose residues are directly united, as they are in disaccharides, for on treatment with the enzyme *maltase*, amygdalin loses one molecule of glucose, being converted into a true glucoside, the glucoside of benzaldehyde cyanohydrin :



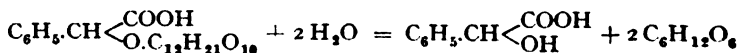
The glucosidic portion of this substance possesses a structure analogous to that of methyl glucoside (p. 276) and may be formulated thus :



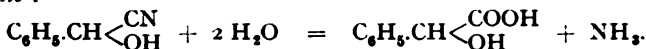
On boiling with dilute alkali, amygdalin is converted into ammonia and an acid called *amygdalinic acid* :



this, on hydrolysis with dilute acids, yields glucose and a hydroxy acid called *mandelic acid* :

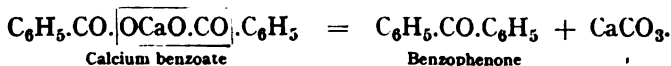


Mandelic acid can also be produced by the hydrolysis of benzaldehyde cyanohydrin, which is for this reason also termed *mandelonitrile* :



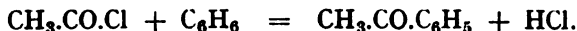
A large number of other glucosides of aromatic hydroxy-compounds are found in nature ; such are *helicin* $\text{CHO.C}_6\text{H}_4\text{.O.C}_6\text{H}_{11}\text{O}_5$ derived from salicylaldehyde ; *salicin* $\text{CH}_2\text{OH.C}_6\text{H}_4\text{.O.C}_6\text{H}_{11}\text{O}_5$, derived from the corresponding alcohol (saligenin, *o*-hydroxybenzyl alcohol $\text{HO.C}_6\text{H}_4\text{.CH}_2\text{OH}$) ; and *arbutin* $\text{HO.C}_6\text{H}_4\text{.O.C}_6\text{H}_{11}\text{O}_5$, derived from hydroquinone (p. 345).

AROMATIC KETONES possess many points of similarity with aliphatic ketones. They may be prepared by the dry distillation of calcium salts :



They react with hydroxylamine and phenylhydrazine, yielding oximes and phenylhydrazones respectively.

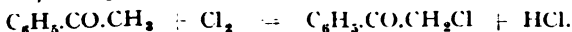
The simplest aromatic ketone is **acetophenone** (*phenyl methyl ketone*), $\text{C}_6\text{H}_5\text{.CO.CH}_3$. This is formed by distilling a mixture of calcium benzoate and calcium acetate (cf. p. 141) ; it is more conveniently prepared by the Friedel-Crafts reaction (p. 322), by causing acetyl chloride to react with benzene in presence of aluminium chloride :



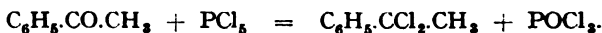
Acetophenone is a colourless substance of characteristic odour. It melts at 20° and boils at 202° . It possesses most of the characteristic chemical properties of aliphatic ketones, forming a cyanohydrin, an oxime, and a hydrazone. It does not, however, combine with sodium hydrogen sulphite. Acetophenone has been employed as a hypnotic, under the name "*Hypnone*."

On oxidation, acetophenone yields benzoic acid ; on reduction it is converted into the corresponding secondary alcohol *phenyl methyl carbinol* $\text{C}_6\text{H}_5\text{.CHOH.CH}_3$.

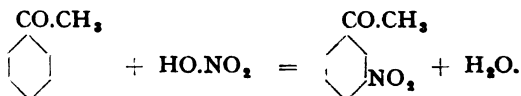
It reacts very readily with chlorine or bromine, yielding *ω*-chloro- (or bromo-) *acetophenone* :



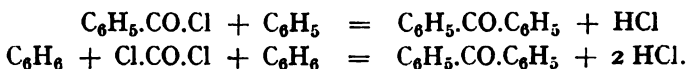
With phosphorus pentachloride, two chlorine atoms take the place of the oxygen atom :



On treatment with cold concentrated nitric acid, *m*-nitroacetophenone is the principal product :

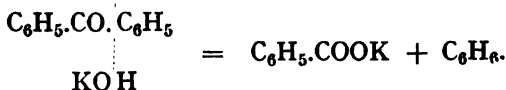


Benzophenone $\text{C}_6\text{H}_5.\text{CO}.\text{C}_6\text{H}_5$ is, as already stated, formed by the distillation of dry calcium benzoate. It is, like acetophenone, more conveniently prepared by the Friedel-Crafts reaction, by the action of a mixture of benzene and aluminium chloride upon either benzoyl chloride (p. 393) or carbonyl chloride :



It is also formed by the oxidation of diphenylmethane (p. 325).

Benzophenone is a colourless crystalline substance which melts at 48° and boils at 306° . On reduction it is converted into *benzhydrol* $\text{C}_6\text{H}_5.\text{CHOH}.\text{C}_6\text{H}_5$; on oxidation, one of the phenyl radicles is destroyed, benzoic acid being formed. On heating with potassium hydroxide, benzophenone is converted into benzene and benzoic acid :



CHAPTER XXXIII

AROMATIC CARBOXYLIC ACIDS

SIMPLE MONOCARBOXYLIC ACIDS

THERE are no essential differences between the reactions of the carboxyl group in aromatic and aliphatic compounds. On comparing benzoic acid with acetic acid, analogous derivatives exist throughout :

$\text{CH}_3\text{.COOH}$	Acid	$\text{C}_6\text{H}_5\text{.COOH}$
$\text{CH}_3\text{.COOK}$	Potassium salt	$\text{C}_6\text{H}_5\text{.COOK}$
$\text{CH}_3\text{.COCl}$	Chloride	$\text{C}_6\text{H}_5\text{.COCl}$
$\text{CH}_3\text{.COOC}_2\text{H}_5$	Ethyl ester	$\text{C}_6\text{H}_5\text{.COOC}_2\text{H}_5$
$(\text{CH}_3\text{.CO})_2\text{O}$	Anhydride	$(\text{C}_6\text{H}_5\text{.CO})_2\text{O}$
$\text{CH}_3\text{.CO.NH}_2$	Amide	$\text{C}_6\text{H}_5\text{.CO.NH}_2$
$\text{CH}_3\text{.C}\equiv\text{N}$	Nitrile	$\text{C}_6\text{H}_5\text{.C}\equiv\text{N}$

In addition to the properties attributed to the carboxylic group, aromatic acids possess the faculty of forming nuclear substitution-products. Here the analogy between acetic and benzoic acids does not apply so accurately ; thus, only one monochloroacetic acid is known, while there are three monochlorobenzoic acids.

Benzoic acid $\text{C}_6\text{H}_5\text{.COOH}$ derives its name from the fact that it was first obtained by heating a resin known as *gum benzoin*, and from this name is derived the multitude of chemical names beginning with the syllable *benz-*.

Another natural source of benzoic acid is the urine of herbivores, which, when allowed to decompose, deposits benzoic acid. This is due to the hydrolysis of the *hippuric acid*

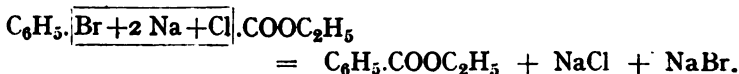


(p. 394), which is present in the urine of all graminivorous animals.

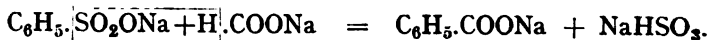
The chief source of benzoic acid at the present day is the toluene obtained from coal-tar (p. 319), from which it is technically prepared by treatment with chlorine, the resulting benzo-trichloride $C_6H_5.CCl_3$ (p. 331) being hydrolysed to benzoic acid by heating with milk of lime. Benzoic acid is also manufactured by oxidising benzyl chloride (p. 331). On a small scale it may be prepared by the hydrolysis of benzonitrile (p. 394).

Benzoic acid is formed by the oxidation of all monosubstituted derivatives of benzene in which a carbon atom is attached to the benzene nucleus. It is produced, for example, by the action of dilute nitric acid upon toluene.

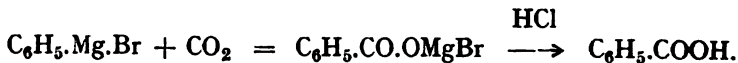
Of theoretical interest are the following methods of formation of benzoic acid. By the action of sodium upon a mixture of bromobenzene and ethyl chloroformate (p. 179), ethyl benzoate is produced in small quantity :



Sodium benzoate is produced on heating a mixture of sodium benzenesulphonate (p. 332) and sodium formate :



Finally, benzoic acid is produced by the action of carbon dioxide upon phenyl magnesium bromide (cf. p. 237) :



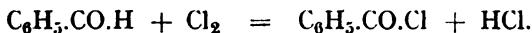
Benzoic acid is a white crystalline solid which melts at 121° and boils at 250° , but sublimes rapidly before fusion. It is volatile with steam; its vapour irritates the mucous-membranes. Benzoic acid is sparingly soluble in cold water, but dissolves readily in hot water.

Esters of benzoic acid may be prepared by heating benzoic acid with an alcohol in presence of dry hydrogen chloride. *Methyl benzoate* boils at 198° , *ethyl benzoate* at 213° . Both are colourless liquids possessing characteristic odours.

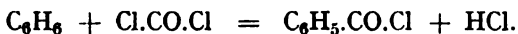
Benzoyl chloride $C_6H_5.COCl$ is generally prepared by the action of phosphorus pentachloride upon benzoic acid :



It is readily produced by the action of chlorine upon benzaldehyde :

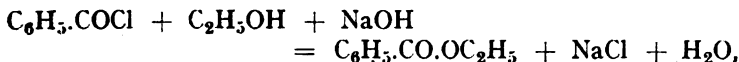


It is also formed by the action of carbonyl chloride (in excess) upon a mixture of benzene and aluminium chloride (cf. p. 390) :



Benzoyl chloride is a colourless liquid, boiling at 198° , the vapour of which is exceedingly irritating. It fumes in moist air, but is decomposed by cold water much more slowly than are the chlorides of fatty acids.

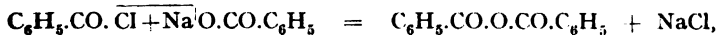
Benzoyl chloride is extensively employed in the laboratory for the benzylation of hydroxylic and amino compounds, the formation of a benzoyl derivative being, like the formation of an acetyl derivative, indicative of the presence of an alcoholic hydroxyl group or of an amino or imino group. Benzylation is usually carried out by the *Schotten-Baumann* method—by shaking the substance to be benzyolated with excess of benzoyl chloride and dilute alkali until the benzoyl chloride has been entirely decomposed :



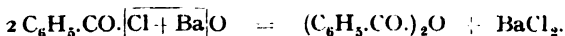
the unused benzoyl chloride yielding sodium chloride and sodium benzoate with the alkali :



Benzole anhydride $C_6H_5.CO.O.CO.C_6H_5$ can be prepared by the action of benzoyl chloride upon sodium benzoate :

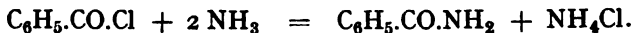


or of barium oxide upon benzoyl chloride at 150° :



Benzoic anhydride is a white solid, melting at 42° , boiling at 360° . It is very stable towards water and aqueous alkalis, being hydrolysed only by boiling with alcoholic alkali. For this reason it is not employed as a benzoylating agent.

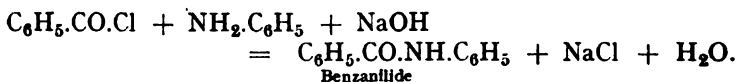
Benzamide $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2$ is formed by the action of benzoyl chloride upon ammonia :



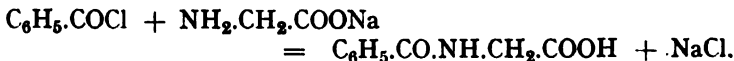
It is a white crystalline solid, which melts at 130° . In properties it is a typical acid amide ; it is hydrolysed on boiling with aqueous acids and alkalis, and on dehydration it yields benzonitrile. On boiling with alkaline hypobromite solution (Hofmann's reaction, p. 200) it is converted into aniline :



Substituted benzamides are produced by treating primary and secondary amines with benzoyl chloride, by the Schotten-Baumann method. Such is **benzanilide** :



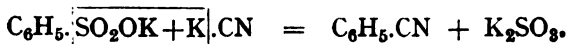
An important derivative of benzamide is **hippuric acid** (*benzoylaminoacetic acid*) $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, to which reference has already been made (pp. 290, 391). It is always present in the urine of herbivorous animals, and can be found in that of carnivorous animals to whom a dose of benzoic acid has been administered. It can be prepared by the action of benzoyl chloride upon glycine (p. 289) in presence of alkali :



and is broken up into glycine and benzoic acid on hydrolysis.

Benzonitrile, *phenyl cyanide*, $\text{C}_6\text{H}_5\cdot\text{C}\cdot\text{N}$, is formed by the action of dehydrating agents, such as phosphorus pentoxide or phosphorus pentachloride, upon benzamide (cf. p. 173). It may also be prepared from aniline by Sandmeyer's reaction

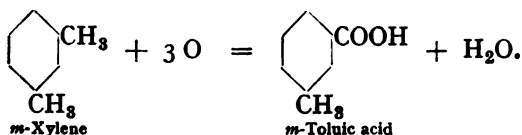
(p. 375), and by heating together potassium benzenesulphonate and potassium cyanide :



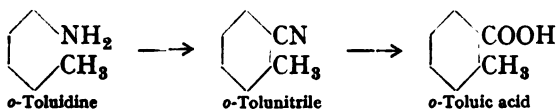
Benzonitrile is a colourless liquid which boils at 191° , is insoluble in water, and has a powerful odour resembling that of benzaldehyde. It is a true nitrile, yielding benzoic acid and ammonia on hydrolysis. On reduction it yields benzylamine (p. 364) :



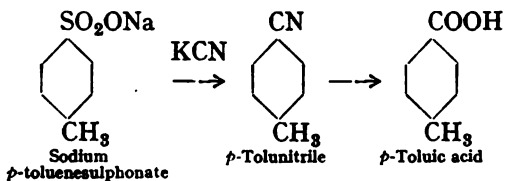
The three **toluic acids** $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ may be prepared by various general methods : (1) by partial oxidation of the corresponding xylenes, *e.g.* :



(2) by hydrolysis of the corresponding tolunitrile, which can be prepared by the Sandmeyer reaction from the corresponding toluidine, *e.g.* :



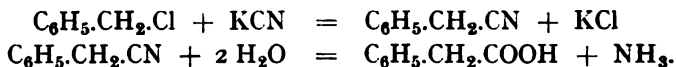
or from the corresponding toluenesulphonic acid (cf. above), *e.g.* :



They all closely resemble benzoic acid in their properties. On distillation with soda-lime (cf. p. 76) they yield toluene.

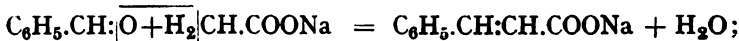
On oxidation they yield the three phthalic acids (pp. 397, 399) respectively.

A fourth isomeric acid is **phenylacetic acid** $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{COOH}$, in which the carboxyl group is attached not to the nucleus, but to the side-chain. Its relation to benzyl chloride (p. 331) is made clear by its synthesis through benzyl cyanide (*phenyl-acetonitrile*) :

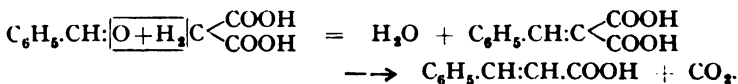


Phenylacetic acid is a white solid, melting at 76° . It can be distilled without decomposition, boiling at 265° . It forms esters, chloride, amide, and other derivatives of the carboxyl group; in addition it possesses the properties of aromatic compounds; it can be nitrated, sulphonated, etc. On oxidation it yields benzoic acid.

Cinnamic acid, *β -phenylacrylic acid*, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, is the acid corresponding with cinnamaldehyde (p. 386). It occurs naturally in certain balsams and resins, such as *storax*. Synthetically it may be prepared by heating a mixture of benzaldehyde, sodium acetate, and acetic anhydride (Perkin's reaction) :



or by warming benzaldehyde and malonic acid together in presence of a little ammonia, and heating the resulting *benzylidene-malonic acid*, which loses carbon dioxide (cf. p. 187) :



It is prepared technically by heating benzal chloride (p. 331) with sodium acetate :



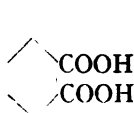
Cinnamic acid is a colourless solid which melts at 133° . It is sparingly soluble in cold water; readily in hot water. With bromine it yields the acid $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COOH}$; on oxidation it yields, according to the oxidising agent, either

β -phenylglyceric acid $C_6H_5.CHOH.CHOH.COOH$, benzaldehyde, or benzoic acid. On reduction by sodium amalgam and water it is converted into **hydrocinnamic acid**, β -phenylpropionic acid, $C_6H_5.CH_2.CH_2.COOH$.

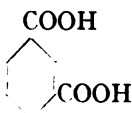
Nuclear-substituted derivatives of cinnamic acid can be prepared. Such are the *nitrocinnamic acids* $NO_2.C_6H_4.CH:CH.COOH$. The *ortho* and *para* derivatives are produced by the action of concentrated nitric acid upon cinnamic acid; *meta* nitrocinnamic acid can be prepared by the action of *m*-nitrobenzaldehyde (p. 387) upon a mixture of sodium acetate and acetic anhydride (Perkin's reaction). Other substituted cinnamic acids may be prepared by heating the corresponding derivative of benzaldehyde with sodium acetate and acetic anhydride.

SIMPLE DICARBOXYLIC ACIDS

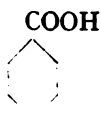
The existence of the three **phthalic acids** has already been mentioned as being produced by the oxidation of the three xylenes (p. 322). They are named as follows :



Phthalic acid



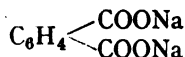
Isophthalic acid



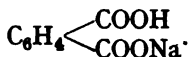
Terephthalic acid

The most important of these is the *ortho* compound, **phthalic acid**. Though, as above remarked, it may be prepared by the oxidation of *o*-xylene (p. 322), or *o*-toluic acid, the chief source is naphthalene (p. 406), which on oxidation yields phthalic acid, and from which the name is derived. This reaction will be discussed when we come to consider the constitution of naphthalene.

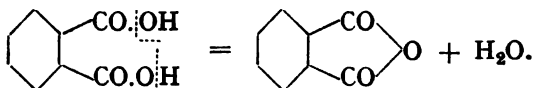
Phthalic acid is a colourless solid, sparingly soluble in cold water, readily in hot water. It is largely employed in the manufacture of the *phthalein* (p. 439) dyes, and in the manufacture of synthetical indigo (p. 445). Like the aliphatic dicarboxylic acids, such as succinic acid (p. 189), it yields neutral salts (*e.g.* sodium phthalate)



and acid salts (e.g. sodium hydrogen phthalate)



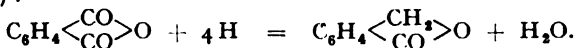
It resembles succinic acid in another feature : when heated it yields up one molecule of water, and is converted into **phthalic anhydride** :



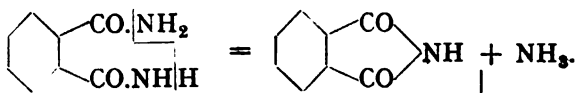
For this reason the melting-point of phthalic acid is indefinite, and depends upon the rapidity of heating.

Phthalic anhydride melts at 128° , and can be obtained in beautiful needles by sublimation. It is hydrolysed very slowly by water ; with alkalis it readily yields phthalates.

On heating with phenol and a little concentrated sulphuric acid, *phenolphthalein* (p. 439) is formed ; heating with resorcinol produces *fluorescein* (p. 441). On reduction, phthalic anhydride is converted into *phthalide*, which is a lactone, or internal ester (p. 246) :



Phthalic acid, on heating with phosphorus pentachloride, is converted into **phthalyl chloride**, which on treatment with ethyl alcohol yields **ethyl phthalate** $\text{C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2$. This, on treatment with ammonia, yields **phthalamide** $\text{C}_6\text{H}_4(\text{CONH}_2)_2$. Phthalamide, like succinamide (p. 191), loses ammonia on heating, and passes into **phthalimide** :

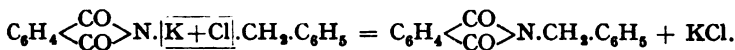


Phthalimide, like succinimide, is endowed with distinct acidic qualities, and yields stable salts with alkali metals.

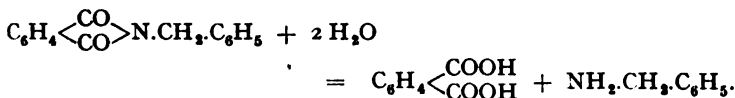


is employed in organic synthesis for the replacement of a halogen atom by a primary amino group. Thus, for example, potassium

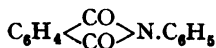
phthalimide yields benzyl phthalimide on treatment with benzyl chloride :



Such substituted phthalimides are hydrolysed on heating with aqueous mineral acids, yielding phthalic acid and primary amines :

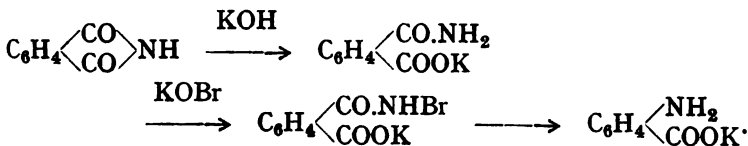


Phthalanil

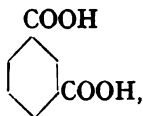


is produced by heating phthalic acid with aniline.

On warming phthalimide with an alkaline solution of a hypobromite, Hofmann's reaction ensues (cf. p. 394), *o*-amino-benzoic acid (anthranilic acid, p. 404) being formed. The changes which take place during this reaction are :

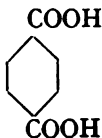


Isophthalic acid



formed by the oxidation of *m*-xylene (p. 422) or of *m*-toluic acid, differs from phthalic acid in being incapable of forming an anhydride or an imide.

Terephthalic acid

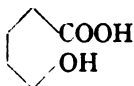


formed by the oxidation of *p*-xylene, resembles isophthalic acid in general properties.

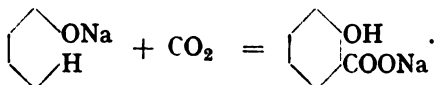
SUBSTITUTED AROMATIC ACIDS

Aromatic hydroxy-acids may be divided into two classes: *phenolic* hydroxy-acids, in which the hydroxyl group is directly attached to the benzene nucleus, and *alcoholic* hydroxy-acids, in which the hydroxyl group is attached to a side-chain.

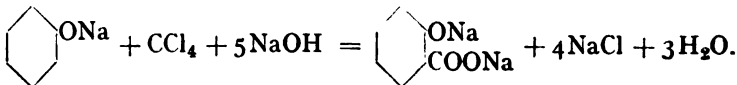
Salicylic acid



is one of the most important of the phenolic hydroxy-acids. It occurs in nature, as the methyl ester, in oil of wintergreen. Synthetically it is prepared by an interesting reaction, known as *Kolbe's reaction*; on heating dry sodium phenoxide in a stream of carbon dioxide, sodium salicylate is formed:



This reaction somewhat resembles Reimer's reaction (p. 387) (the formation of salicylaldehyde by the action of chloroform upon an alkaline solution of phenol), and indeed salicylic acid is formed in an analogous manner by heating an alkaline solution of phenol with carbon tetrachloride:



a greater proportion of *p*-hydroxybenzoic acid (p. 402), however, is formed by this method.

Salicylic acid may of course also be prepared by the diazotisation of anthranilic acid (p. 404), or by the hydrolysis of the *ortho* hydroxy derivative of benzonitrile, as well as by the oxidation of salicylaldehyde.

It is a colourless crystalline substance, which melts at 159°. It possesses phenolic properties, and develops, in dilute aqueous solution, a violet coloration on addition of ferric chloride.

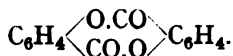
On account of its bactericidal properties it finds wide application as a preservative for foods, though it is undecided whether this use may not be harmful to the human organism.

Salicylic acid behaves as a carboxylic acid in that it forms esters. The methyl ester $\text{HO.C}_6\text{H}_4.\text{COOCH}_3$, which, as mentioned above, is the odorous principle of oil of wintergreen, is a fragrant liquid which boils at 224° ; the phenyl ester

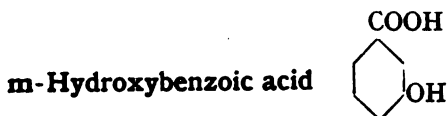


is a solid melting at 42° , which is employed medicinally under the name "salol."

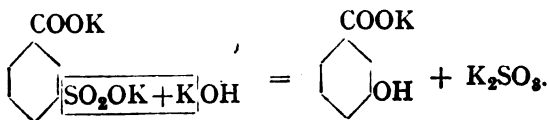
On the other hand, the hydroxylic character of salicylic acid shows itself in its faculty for forming acyl derivatives. Thus *acetylsalicylic acid* $\text{CH}_3.\text{CO}.\text{OC}_6\text{H}_4.\text{COOH}$, a white solid which melts at 135° , is produced by the action of acetic anhydride upon salicylic acid. It is widely employed as an analgesic under the proprietary name "Aspirin." A compound analogous to lactide (p. 244) can be obtained from salicylic acid; this is *disalicylide*

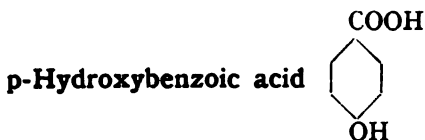


On treating an alkaline solution of sodium salicylate with methyl sulphate or methyl iodide, *o-methoxybenzoic acid* (*methylsalicylic acid*) $\text{CH}_3\text{O.C}_6\text{H}_4.\text{COOH}$ is produced.



is an unimportant substance, best obtained by fusing *m*-sulphobenzoic acid—the product of sulphonation of benzoic acid (p. 403)—with potassium hydroxide:



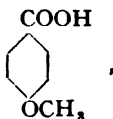


may be prepared by oxidation of *p*-cresol. It is also formed by heating dry potassium phenoxide in an atmosphere of carbon dioxide, and is the chief product of the interaction of carbon tetrachloride with an alkaline solution of phenol (p. 400).

It is interesting to note that potassium *p*-hydroxybenzoate is produced by intramolecular change on heating potassium salicylate to 210-220°. Sodium salicylate does not undergo this change; on the contrary, on heating sodium *p*-hydroxybenzoate to 290°, sodium salicylate is formed.

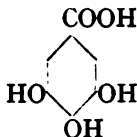
Neither *para* nor *meta* hydroxybenzoic acid possess the bactericidal properties of salicylic acid, nor do they develop a violet coloration in aqueous solution with ferric chloride.

The most important derivative of *p*-hydroxybenzoic acid is **anisic acid** (*p*-methoxybenzoic acid)



which is produced by the oxidation of anethole or anisaldehyde (p. 387). It is formed by the methylation of *p*-hydroxybenzoic acid.

Of the polyhydroxylic derivatives of benzoic acid the most important is **gallic acid**

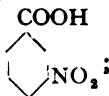


which occurs in certain plants, and is prepared by boiling tannin with dilute sulphuric acid. On heating, it loses carbon dioxide, pyrogallol (p. 348) being formed.

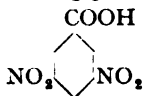
The simplest example of an *alcoholic* aromatic hydroxy-acid

is **mandelic acid** (*phenylglycollic acid*) $C_6H_5.CHOH.CO_2H$, which behaves as a true aliphatic hydroxy-acid. Its modes of formation from benzaldehyde cyanohydrin (p. 385) and from amygdalin (p. 388) have already been mentioned. It contains an asymmetric carbon atom, and can be obtained in two stereoisomeric optically active varieties. The racemic form is of course produced by the synthetical methods of formation.

Benzoic acid, on nitration, yields *m*-nitrobenzoic acid

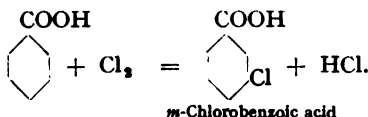


the *ortho* and *para* nitrobenzoic acids may be obtained by oxidation of the *ortho* and *para* nitrotoluenes (p. 351) respectively. On further nitration of benzoic acid, 3,5-dinitrobenzoic acid



is produced.

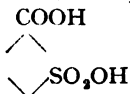
Similarly, on treating benzoic acid with halogen, the *meta* derivative is produced :



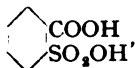
m-Chlorobenzoic acid

The *ortho* and *para* derivatives are obtained either by oxidation of the corresponding derivative of toluene, or by conversion of a halogen-substituted amine into the cyanide by means of Sandmeyer's reaction (p. 375), with subsequent hydrolysis.

On sulphonating benzoic acid, *m*-sulphobenzoic acid

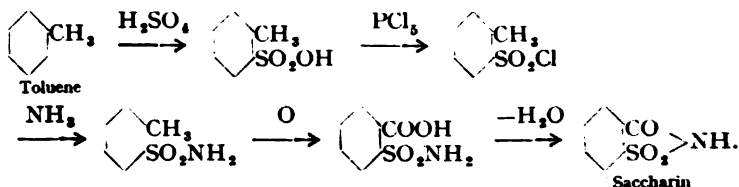


is formed ; the *ortho* and *para* sulphobenzoic acids are readily obtained by oxidising the corresponding toluenesulphonic acids, both of which are formed of sulphonation of toluene. Of chief interest is *o*-sulphobenzoic acid

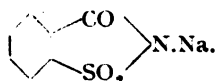


since its *imide* is of great technical importance.

This is "saccharin"; owing to its intensely sweet taste, it is employed by diabetics as a substitute for sugar. It is prepared technically by the following series of steps :

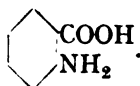


Saccharin is but sparingly soluble in water, but since a 0.02 per cent. aqueous solution tastes as sweet as a 10 per cent. solution of cane sugar, there is little necessity for great solubility. As may readily be understood, saccharin possesses marked salt-forming properties, and yields with sodium hydroxide a compound



This sodium derivative crystallises with two molecules of water, and is more readily soluble than the free saccharin; since it also possesses the sweet taste of saccharin, it is often employed as a sweetening agent.

On reducing nitrobenzoic acids, **aminobenzoic acids** are formed. The most important of these is *o*-aminobenzoic acid, generally called **anthranilic acid**



This may be formed by the reduction of *o*-nitrobenzoic acid, but the technical method of preparation consists in treating phthalimide with alkaline hypochlorite or hypobromite (p. 399). It is a very weakly acid compound, due to the neutralisation of the acidic radicle of the basic amino group, and may, like glycine (p. 289), be regarded as an inner salt. It forms esters with alcohols; it also forms salts with strong acids, such as hydrochloric acid.

Anthranilic acid undergoes all the typical reactions of an aromatic primary amine: thus on diazotisation and boiling

it yields salicylic acid; *ortho*-halogen-substituted derivatives of benzoic acid may be produced by Sandmeyer's reaction; whilst reduction of the diazo derivative in alkaline solution leads to benzoic acid. On treatment with acetic anhydride it is converted into *acetylanthranilic acid* :



Aromatic amino-acids are also known, in which the amino group is attached to the side chain. Notable members of this class are **phenylalanine** $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}$ and its *p*-hydroxy derivative **tyrosine**

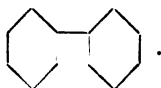


These two amino-acids occur, in a combined form, in proteins (see p. 295), both being optically active.

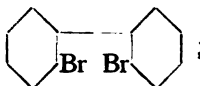
CHAPTER XXXIV

CONDENSED BENZENOID SYSTEMS

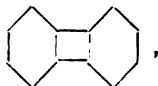
IN the chapter on aromatic hydrocarbons it was noted that compounds can exist in which two or more benzene nuclei are present. Such is **diphenyl**



Two benzene nuclei can also be united at two points: if diphenyl be brominated, a dibromodiphenyl can be isolated from the reaction products in which both bromine atoms are in the *ortho* positions



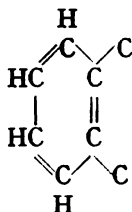
if this substance be treated with sodium, a new hydrocarbon, **diphenylene**



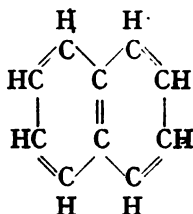
is formed. In both diphenyl and diphenylene the two benzene nuclei are directly *joined*; these substances do not come into the purview of this chapter. To explain the term "condensed" (or "co-ordinated") as applied to benzene nuclei, we must now discuss the constitution of **naphthalene**.

Naphthalene is a hydrocarbon obtained from coal tar, the empirical formula of which is $C_{10}H_8$. In chemical character it closely resembles benzene. On vigorous oxidation it yields

phthalic acid (p. 397) ; this fact showing it to be derived from benzene, and to contain two carbon atoms attached to the benzene nucleus in the *ortho* position :



We can thus so far account for eight carbon atoms and four hydrogen atoms, leaving undetermined the positions of two carbon atoms and four hydrogen atoms. Now since naphthalene possesses properties similar to those of benzene, and is not very readily attacked by oxidising agents, it would appear that the disposition of its constituent atoms cannot be in the form of unsaturated open chains, but rather that they are so distributed as to render them comparable to those of benzene. This constitution may be expressed thus :



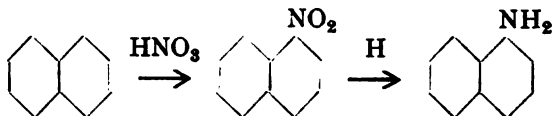
In this arrangement, which may be compared to that of the Siamese twins, two benzenoid systems, having two atoms of carbon in common, share certain portions of their structure.

The formula for naphthalene is usually abbreviated to :

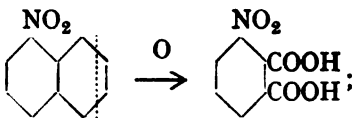


That both halves of the molecule are really aromatic in character is shown by the following facts : naphthalene, on

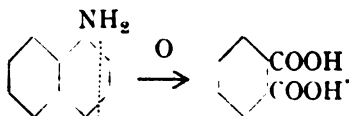
nitration, yields a mononitro derivative which on reduction yields the corresponding amino compound :



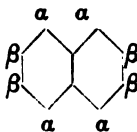
The nitronaphthalene, on oxidation, yields a nitrophthalic acid :



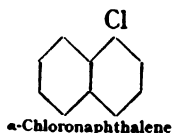
the above-mentioned aminonaphthalene, on the other hand, yields phthalic acid on oxidation :



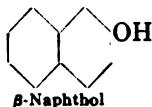
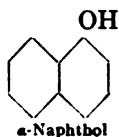
There is another important piece of evidence tending to establish the correctness of the above view, and this is that two distinct series of monosubstitution-products of naphthalene are known. A glance at the formula for naphthalene will show that two sets of four hydrogen atoms, different in relative position in the structure, can exist. These we designate by the letters α and β :



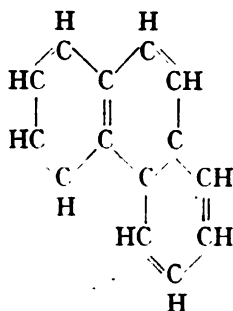
In accordance with this, naphthalene yields the two series—differentiated by the prefixes α and β —of monosubstituted derivatives. Such for example are α -chloronaphthalene and β -chloronaphthalene :



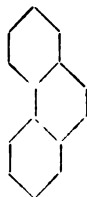
corresponding respectively with the phenolic hydroxy compounds α -naphthol and β -naphthol :



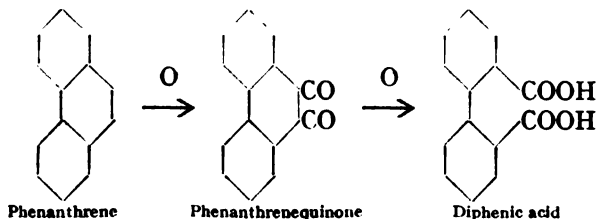
Compounds containing more than two condensed aromatic systems are known ; such are phenanthrene and anthracene. **Phenanthrene** consists of two benzene nuclei condensed with a third one, or of a benzene nucleus condensed with a naphthalene nucleus :



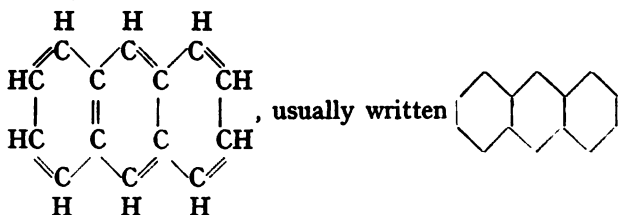
, generally abbreviated to



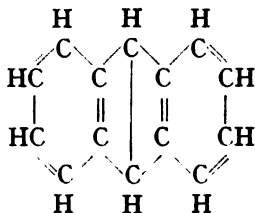
On oxidation, phenanthrene first yields the diketonic compound phenanthrene quinone, while on further oxidation it yields diphenic acid, a dicarboxylic acid derived from diphenyl :



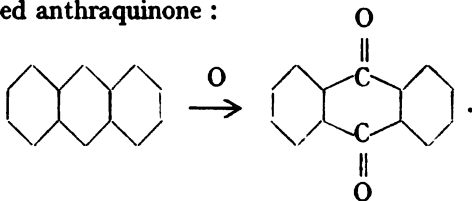
In **anthracene** three benzene nuclei are condensed in a different manner :



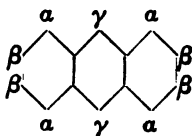
It is, however, generally accepted that the constitution of anthracene may equally well be expressed by a formula in which the central carbon atoms are represented as being directly united :



and for all purposes both formulæ are regarded as synonymous. On oxidation, anthracene is converted into a diketonic compound termed anthraquinone :



Anthracene yields three sets of monosubstitution products, designated α , β , and γ , respectively. This will be understood on reference to the formula :

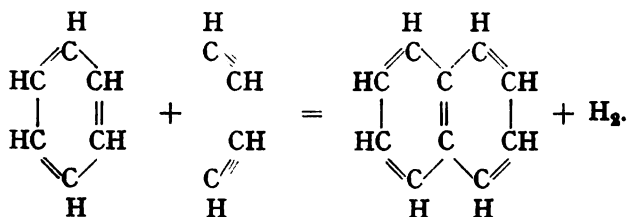


NAPHTHALENE AND ITS DERIVATIVES

Naphthalene is a colourless, crystalline solid of characteristic odour, which melts at 80° and boils at 218° . It readily sublimes at a comparatively low temperature, advantage of this fact being taken for its purification. It is one of the most important and abundant of the constituents of coal tar, and is technically prepared in enormous quantity, being principally employed for the manufacture of dyestuffs. It is also employed for the destruction of moths in clothing.

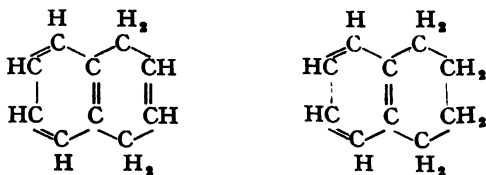
The naphthalene is isolated from coal tar by chilling the fractions boiling between 150° and 270° (see p. 319) and separating the solids which crystallise out. These are then warmed with a small quantity of concentrated sulphuric acid, which converts the impurities into non-volatile sulphonic acids; whereupon the naphthalene, which is not so readily sulphonated, is sublimed or distilled in a current of steam.

Naphthalene may be synthesised by passing a mixture of acetylene and benzene through a heated tube, a reaction recalling the formation of benzene from acetylene alone (p. 317):

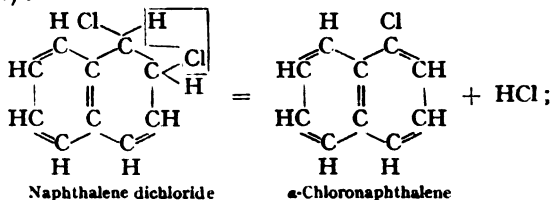


Naphthalene forms with picric acid a characteristic crystalline compound which is sparingly soluble in alcohol.

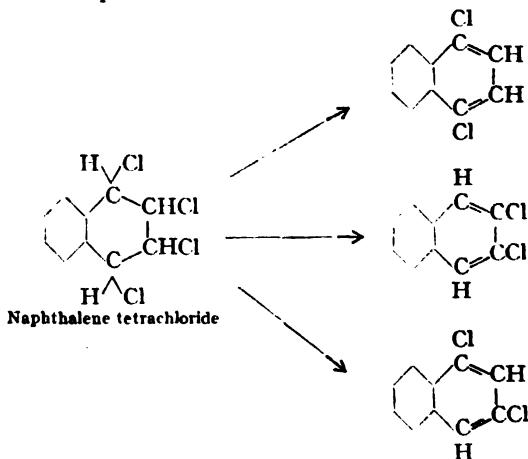
The addition of hydrogen or halogen takes place rather more readily with naphthalene than it does with benzene. The products of hydrogenation are *dihydronaphthalene* and *tetrahydronaphthalene*:



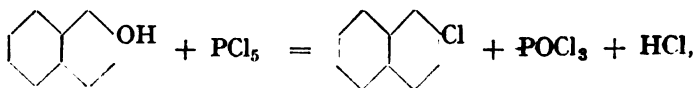
The chlorine addition-products are *naphthalene dichloride* and *naphthalene tetrachloride*, which lose hydrogen chloride on heating, yielding chloroderivatives of naphthalene. Naphthalene dichloride, on heating to 40-50°, yields exclusively α -chloronaphthalene (see below) :



naphthalene tetrachloride, on the other hand, yields a mixture of three dichloronaphthalenes :

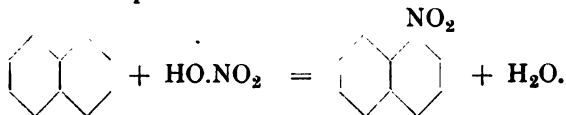


Of the **chloronaphthalenes**, only the α -compound is produced by the chlorination of naphthalene. It is a colourless liquid which boils at 263°. β -chloronaphthalene can be obtained only by an indirect method, such as the action of phosphorus pentachloride upon β -naphthol (p. 414) :



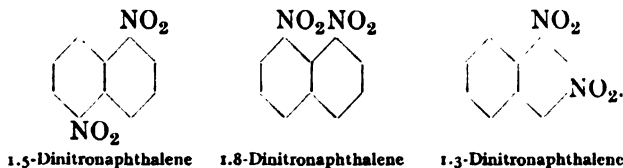
or by the Sandmeyer reaction (p. 375) upon β -naphthylamine (p. 415). It is a solid, melting at 56° and boiling at 265° .

In the same way, only α -nitronaphthalene is formed by the nitration of naphthalene :

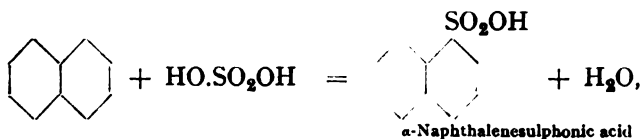


The β -nitronaphthalene can be prepared only by indirect methods, the chief of which is by the action of potassium nitrite upon a mixture of diazotised β -naphthylamine and a cuprous salt.

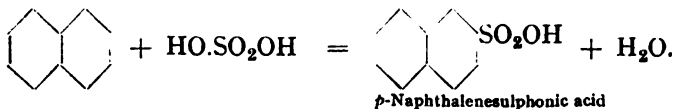
On further nitration, α -nitronaphthalene yields a mixture of three dinitronaphthalenes :



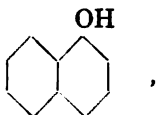
Both naphthalenesulphonic acids are formed on heating naphthalene with concentrated sulphuric acid ; the α -compound is the chief product on heating the mixture at 80° :



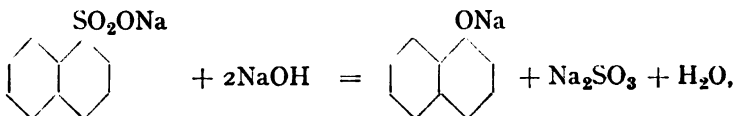
whilst the β -compound is exclusively produced at 160° :



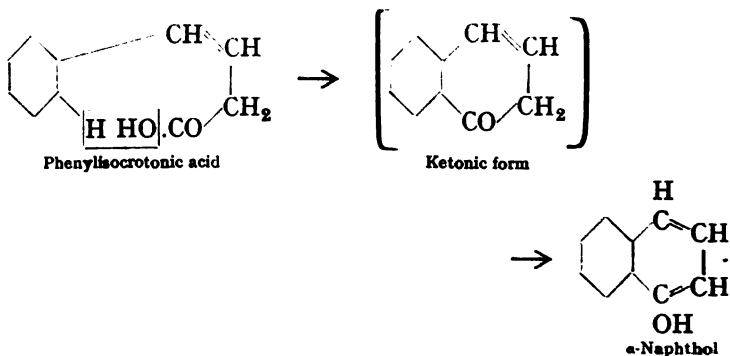
These acids resemble benzenesulphonic acid (p. 332) in general properties. On fusion with alkalis they yield the corresponding naphthols.

α -Naphthol

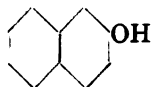
prepared by fusing α -naphthalenesulphonic acid with alkali :



is a colourless solid of phenolic properties which melts at 94° and boils at 279° . An interesting synthesis of α -naphthol has been effected by heating phenylisocrotonic acid :



Nitro derivatives of α -naphthol are formed on nitration ; some of these—particularly the 2.4-dinitro derivative (p. 432), are employed as yellow dyestuffs.

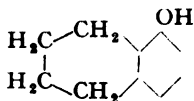
 β -Naphthol

is a compound of similar properties, which melts at 122° and boils at 285° .

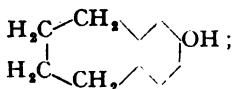
The sulphonic acid derived from the naphthols are largely employed in the manufacture of dyestuffs, since they yield water-soluble azo dyestuffs on treatment with diazo compounds (p. 431).

The hydrogenation of the two naphthols leads to interesting

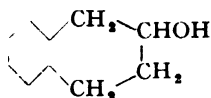
results. Both form tetrahydro derivatives: α -naphthol yields a compound



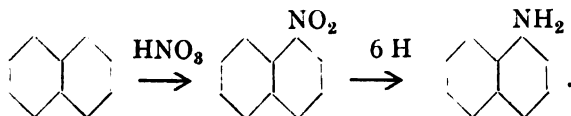
which behaves in every way like a phenol; β -naphthol, on the other hand, yields a mixture of two tetrahydro derivatives, one of which possesses phenolic properties (it is a crystalline solid, insoluble in water, but soluble in dilute alkali), and has the structure



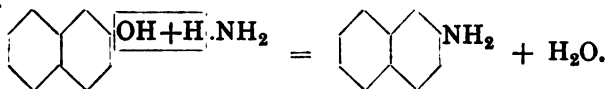
the other behaves in every way like an alcohol (it is a colourless liquid, entirely devoid of acidic properties), and possesses the constitution expressed by :



The naphthylamines may be prepared by the reduction of the corresponding nitronaphthalenes, but this method of preparation is suitable only in the case of α -naphthylamine, for β -nitronaphthalene is not formed by the nitration of naphthalene :



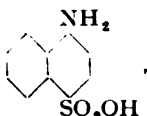
β -Naphthylamine is prepared by heating β -naphthol to 200—210° with the double compound of ammonia and zinc chloride :



The naphthylamines are aromatic primary amines which resemble aniline in chemical character. α -Naphthylamine is a colourless solid of extremely unpleasant odour ; it melts at 50°

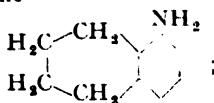
and boils at 301° . β -Naphthylamine possesses only a faint odour ; it melts at 112° and boils at 306° .

The sulphonic acids derived from the naphthylamines are employed in the manufacture of dyestuffs. Typical of these is the analogue of sulphanilic acid, *naphthionic acid*

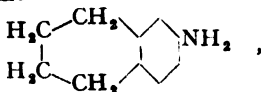


which is prepared by heating α -naphthylamine with sulphuric acid.

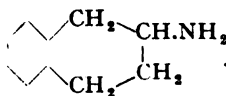
The naphthylamines show the same relations as the naphthols on hydrogenation: α -naphthylamine yields only an aromatic tetrahydronaphthylamine



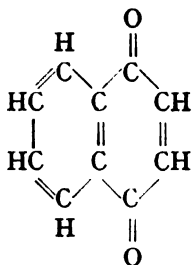
β -naphthylamine yields a mixture of a weakly basic aromatic tetrahydronaphthylamine



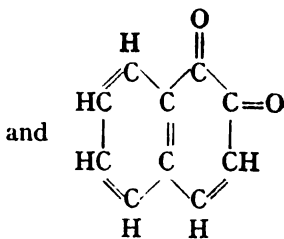
and a strongly basic aliphatic primary amine



As in the case of benzene (pp. 346, 347), two quinones can be derived from naphthalene. These are :

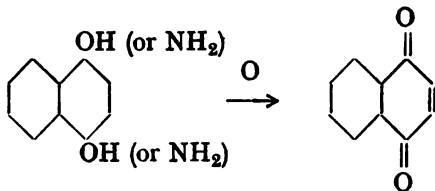


α -Naphthaquinone



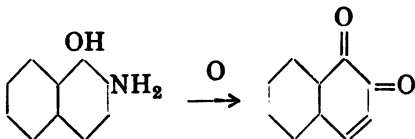
β -Naphthaquinone

The *para* quinone, **α -naphthaquinone**, is produced by oxidising α -naphthylamine, or better 1,4-diaminonaphthalene, 1,4-dihydroxynaphthalene, or 1,4-aminonaphthol:



It is a yellow crystalline substance which melts at 125° . It can be reduced to the corresponding dihydroxy compound, but less readily so, than is *p*-benzoquinone.

The *ortho* quinone, **β -naphthaquinone**, is obtained by oxidising 2-amino- α -naphthol:



It is a red crystalline solid, which decomposes at $115-120^{\circ}$.

Homologues of naphthalene can be produced from naphthalene by the same methods (pp. 321, 322) as those by which the homologues of benzene can be obtained from benzene. **α -Methylnaphthalene** is a liquid boiling at 240° , **β -methylnaphthalene** melts at 32° and boils at 241° .

On oxidation they yield the corresponding **naphthoic acids**, which may also be prepared from the naphthylamines by Sandmeyer's reaction, through the nitriles (cf. p. 395). α -Naphthoic acid melts at 160° ; β -naphthoic acid melts at 182° . These acids closely resemble benzoic acid in chemical character.

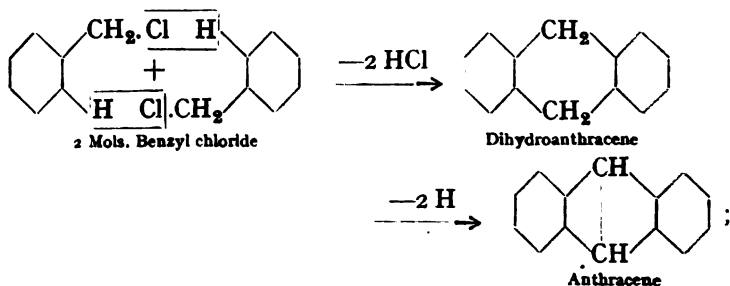
ANTHRACENE AND ITS DERIVATIVES

Anthracene (from $\alpha\nu\theta\rho\alpha\xi$, coal) has already been mentioned (p. 319) as forming a constituent of the higher fractions

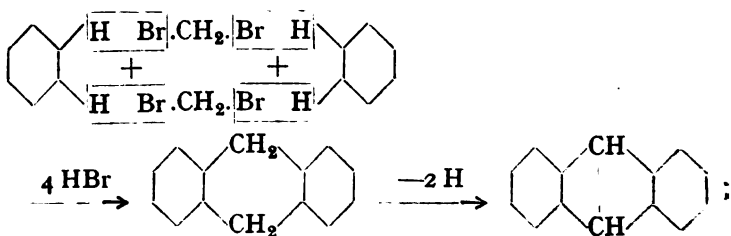
of coal tar. It is a colourless solid which melts at 216° and boils at about 360° , suffering at the same time partial decomposition.

Coal-tar contains only a small proportion (0.25-0.45 per cent.) of anthracene, which is deposited, together with phenanthrene and carbazole (p. 459), on cooling, the fraction boiling above 270° . This crude product is first freed from carbazole, which possesses weakly acidic properties, by distilling with solid potassium hydroxide. The phenanthrene is removed by treatment with carbon disulphide or a mixture of the higher homologues of benzene, in which the anthracene is less soluble. A more profitable method of purification is to recrystallise the crude mixture from a mixture of pyridine (p. 455) and its homologues; this liquid readily dissolves the phenanthrene and carbazole, leaving the anthracene undissolved. Anthracene can be obtained in a state of absolute purity, however, only by distilling anthraquinone with zinc dust.

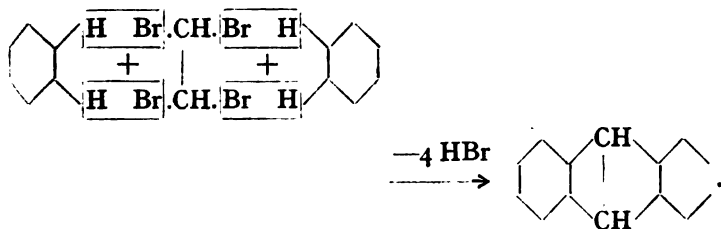
Like naphthalene, anthracene forms a characteristic compound with picric acid. It may be synthesised by heating benzyl chloride with aluminium chloride :



by heating a mixture of methylene bromide and benzene with aluminium chloride :

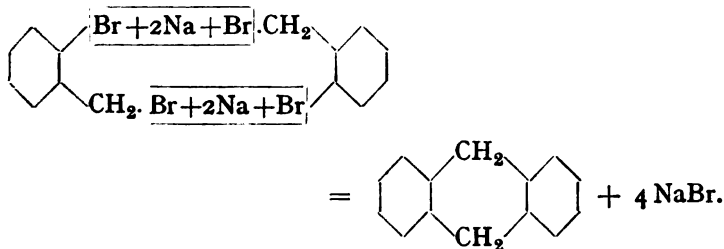


or by heating benzene, acetylene tetrabromide, and aluminium chloride :



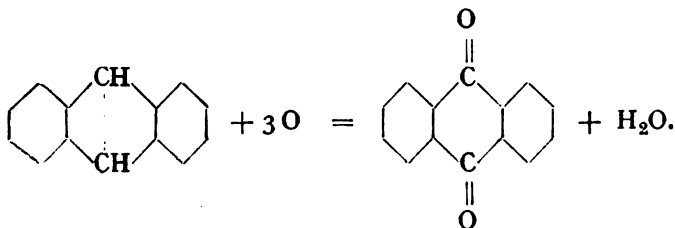
These syntheses, while not forming convenient methods of preparing anthracene, serve to establish its constitution.

Anthracene, on treatment with sodium in boiling alcoholic solution, takes up two hydrogen atoms, yielding *dihydroanthracene*. This substance may be synthesised by treatment of *o*-bromobenzyl bromide with sodium :

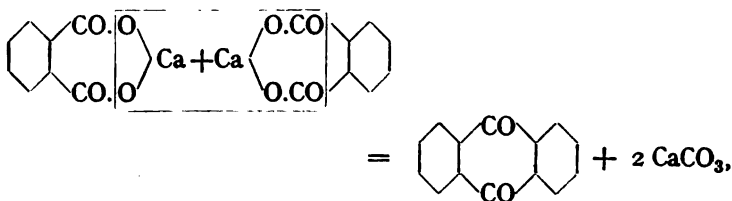


It readily loses these two atoms of hydrogen, being reconverted into anthracene.

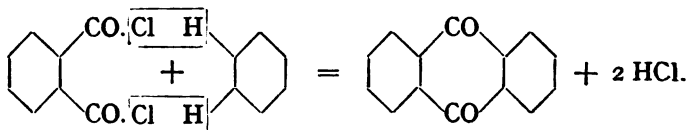
The most important derivative of anthracene is the product it yields on oxidation, **anthraquinone** :



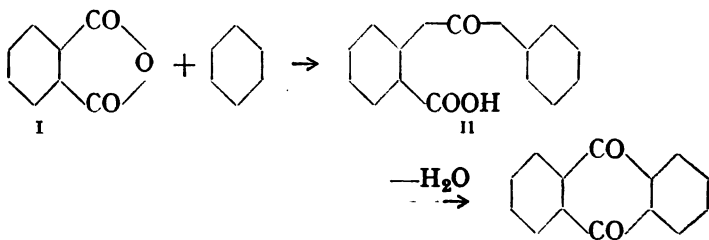
This can be synthesised by heating calcium phthalate :



and is formed by heating a mixture of phthalyl chloride (p. 398) and benzene with aluminium chloride :

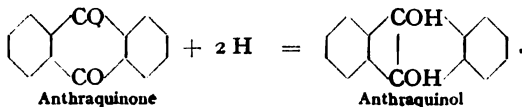


The only synthesis, however, which affords a good yield is the following : phthalic anhydride (I.), on heating with benzene and aluminium chloride, yields *o*-benzoylbenzoic acid (II.) ; this, on warming with concentrated sulphuric acid, readily loses water, yielding anthraquinone :

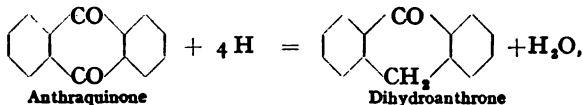


Anthraquinone, usually prepared by the oxidation of anthracene, is a yellow crystalline substance which melts at 284° and boils at 382° ; it sublimes readily on heating. It is insoluble in water, and not very readily soluble in organic liquids, among which hot benzene and glacial acetic acid are the most suitable solvents. It dissolves unchanged in concentrated sulphuric acid, and this solution may be heated to 100° without sulphonation taking place. It is extremely stable towards oxidising agents.

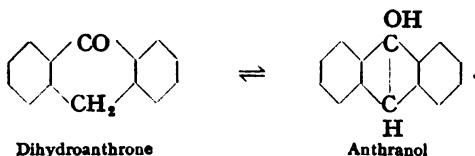
On reduction by alkaline reagents, anthraquinone yields the corresponding dihydroxy compound *anthraquinol* :



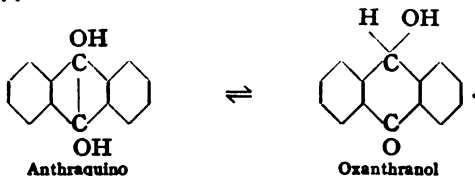
Reduction in acid solution leads to the formation of *dihydroanthrone* :



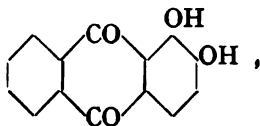
which, on treatment with alkalis, undergoes rearrangement to the phenolic compound *anthranol*. This last substance, on warming alone or with acids, is reconverted into dihydroanthrone :



A similar phenomenon is observed with anthraquinol, which is found to be mutually interconvertible with the ketonic alcohol *oxanthranol* :



The most important derivative of anthraquinone is the dyestuff *alizarin*



an account of which is given on p. 442

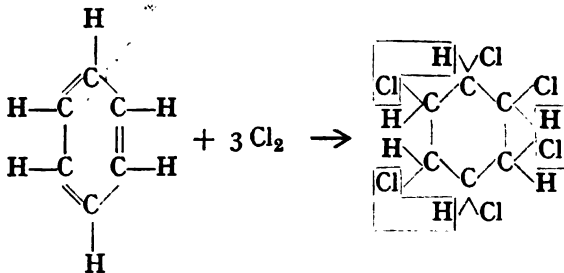
CHAPTER XXXV¹

MECHANISM OF SUBSTITUTION IN AROMATIC COMPOUNDS

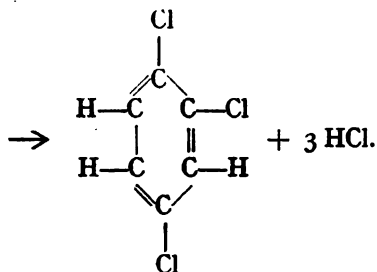
IN the chapter (XXIV) devoted to the general status of aromatic compounds in organic chemistry reference was made to the rules of substitution ; it was shown how the position in the benzene ring taken up by an entering atom or group depends upon the nature of the substituents already present in the molecule.

Having now examined a few cases of substitution in benzene derivatives, it may be well to form some general conclusions, and thus link together, so far as possible, the isolated phenomena hitherto discussed.

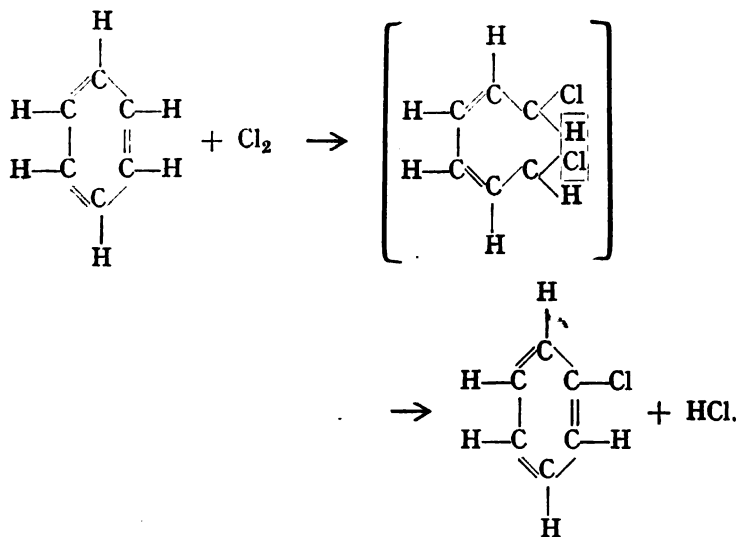
One of the simplest cases of substitution in the aromatic series is the chlorination of benzene. It has already been stated (p. 305) that benzene can, on treatment with chlorine under certain circumstances, form a hexachloro addition-product $C_6H_6Cl_6$; this, on heating, loses hydrogen chloride yielding 1,2,4-trichlorobenzene :



¹ This and the succeeding chapters are beyond the requirements of medical curricula.



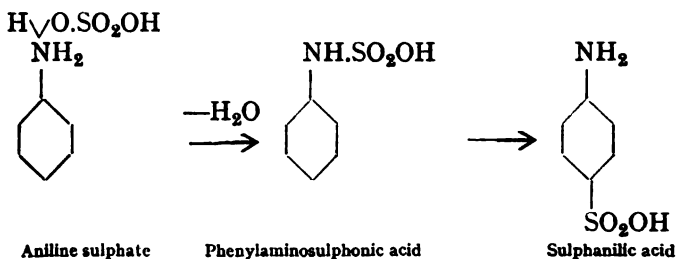
In the same way it is conceivable that under the conditions in which monochlorobenzene is formed, an addition-product is momentarily produced, this breaking down immediately after its formation :



The chlorination of benzene may thus be regarded as the addition of chlorine immediately followed by the elimination of hydrogen chloride. The other types of substitution—bromination, nitration, sulphonation—may be supposed to follow a similar course.

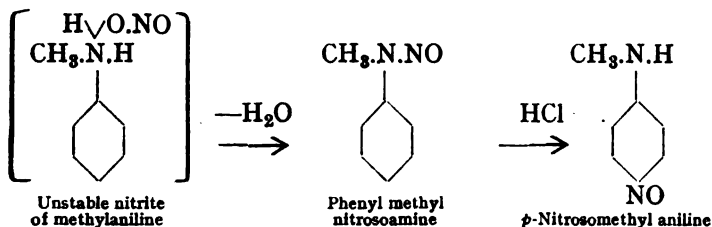
Now certain substituted derivatives of benzene, notably those, like aniline or phenol, which contain radicles *which direct entrant groups to the ortho or para positions* (compare the Crum-Brown rule, p. 315), are more readily affected by substituting agents than is benzene; here the reaction follows a somewhat different course. On the other hand, derivatives of benzene into which new substituent groups enter in the *meta* position—such as nitrobenzene, benzoic acid, or benzenesulphonic acid—react no more readily towards substituting agents than does benzene.

Aniline, on treatment with sulphuric acid, first forms an addition product—aniline sulphate. This, on heating, loses water, phenylaminosulphuric acid being formed, which then undergoes intramolecular rearrangement, the $\text{—SO}_2\text{OH}$ group passing from the nitrogen atom to the benzene nucleus :



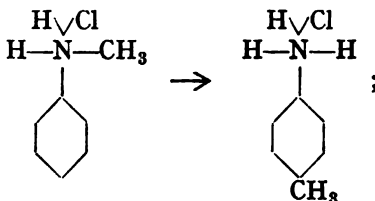
As in the case of benzene, an addition-product is first formed, which passes into a substitution-product; but in this case the addition and elimination takes place exclusively at the nitrogen atom. The substitution in the benzene nucleus then takes place by wandering of the sulphylic group.

Many examples of such migrations of groups from the nitrogen atom into the benzene nucleus are known. Monomethylaniline, on treatment with nitrous acid, first forms a nitrite; this at once loses water, yielding phenyl methyl nitrosoamine (p. 365). If this nitrosoamine be treated with hydrogen chloride, the nitroso (—NO) group migrates into the *para* position :

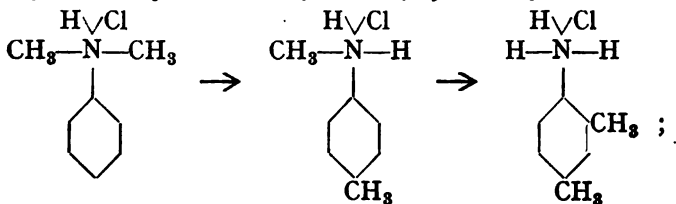


When dimethylaniline is treated with nitrous acid, no nitrosoamine can be formed, and the nitrite passes at once into the *p*-nitroso derivative (p. 367).

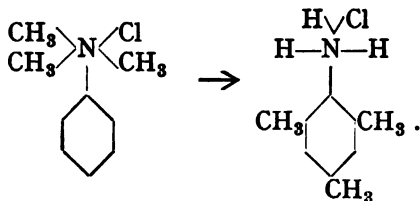
The methyl group itself is capable of wandering from the nitrogen atom into the benzene nucleus. On heating monomethylaniline hydrochloride to 250–350°, *p*-toluidine is quantitatively produced :



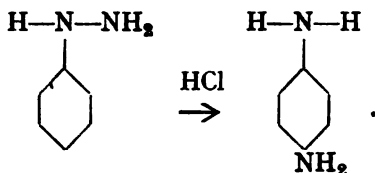
dimethylaniline hydrochloride yields 2,4-xylylidine hydrochloride :



whilst trimethylphenylammonium chloride yields mesidine hydrochloride :

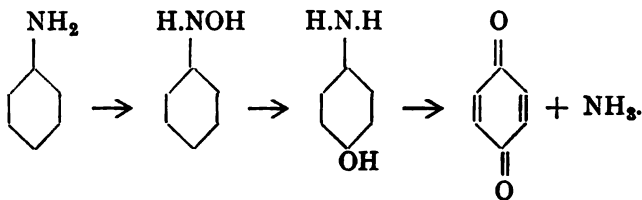


Another example of such rearrangements is the change of phenylhydrazine into *p*-phenylenediamine (p. 383) :

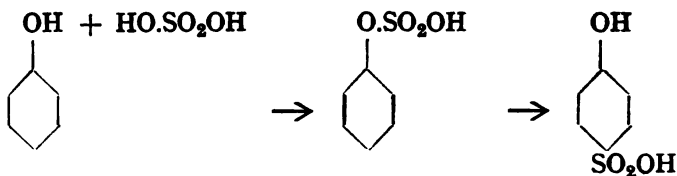


Similar to this are the change from diazoaminobenzene into aminoazobenzene (p. 382), and the conversion of hydrazobenzene into benzidine (p. 383).

The only other example that need here be quoted is the action of oxidising agents upon aniline. It will be recalled that quinone (p. 347) is the final product of this reaction, which however takes place in several stages. The first is the formation of phenyl-hydroxylamine (p. 356) ; this is unstable in presence of either acid or alkali, and passes at once into *p*-aminophenol which undergoes further oxidation :

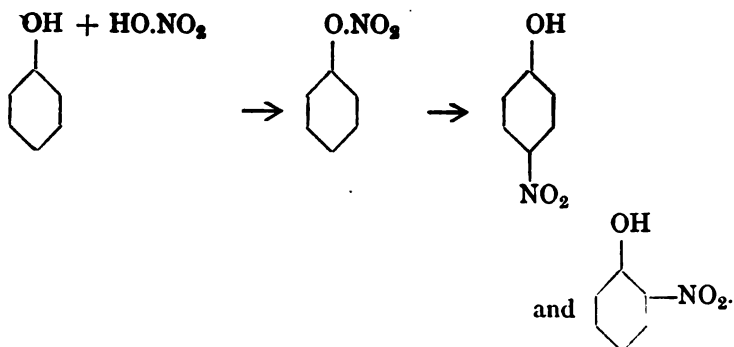


To turn now to phenol ; the sulphonation of phenol (p. 341), which is effected with far greater ease than the sulphonation of benzene, consists in the initial formation of phenylsulphuric acid, with rearrangement of this to *p*-phenolsulphonic acid :

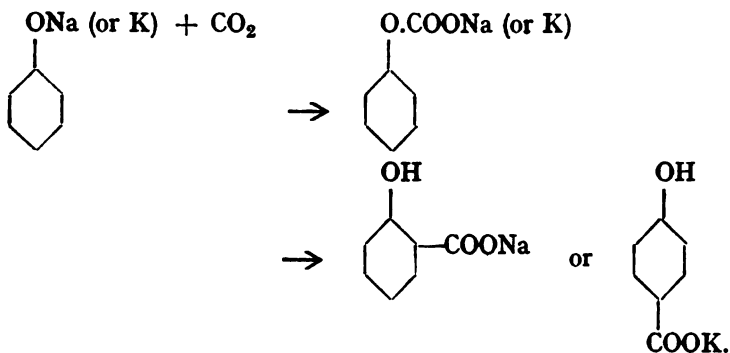


a reaction analogous to the formation of sulphanilic acid.

Nitration may be regarded as taking place in an analogous manner :



The production of salicylic acid and *p*-hydroxybenzoic acid likewise takes place in two stages: the first of these is the formation of a salt of phenylcarbonic acid, which, under the conditions under which it is formed, suffers intramolecular rearrangement :



The formation of these acids by the interaction of an alkaline solution of phenol and carbon tetrachloride presumably follows the same course, as does also the analogous Reimer's reaction (p. 387) for the preparation of hydroxybenzaldehydes by the action of chloroform upon a solution of phenol in alkali.

We have thus seen that the increased reactivity of the derivatives of benzene into which further substituents enter in the *ortho* or *para* positions may be ascribed to the formation of intermediate products which immediately undergo isomeric change. It is, however, probable that some other, as yet un-elucidated, factor enters into the question. It has been noted that the reactivity of derivatives of benzene containing substituents the directing influence of which is to the *meta* position does not exceed that of benzene itself; nevertheless such substituents exercise a marked effect upon atoms or groups situated in certain positions in the same molecule. The nitro group, which directs entrant groups into the *meta* position, may be considered as an example.

The bromine atom in bromobenzene is firmly bound to the nucleus, and is not removed by boiling with alcoholic potash or ammonia. When nitrobenzene is brominated, the resulting *m*-bromo-nitrobenzene is equally stable towards alkalis. Now when bromobenzene is nitrated, *ortho* and *para* bromonitrobenzenes are formed, and in these compounds, the bromine atom is as reactive as in alkyl bromides:—on boiling with alkalis, the bromine is exchanged for hydroxyl; on treatment with ammonia, nitroanilines are produced (pp. 352, 371). Similarly, *m*-nitroaniline is stable towards boiling alkali, whilst *o*- and *p*-nitroanilines are decomposed, yielding ammonia and nitrophenols.

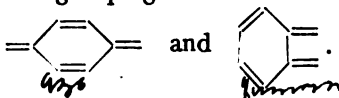
These generalisations have here been introduced, as they not only afford food for reflection, but assist the student to co-ordinate the various phenomena of substitution in derivatives of benzene and the chemical behaviour of the resulting compounds.

CHAPTER XXXVI

CHIEF CLASSES OF DYESTUFFS

ORGANIC dyestuffs are divided in practice into two classes : those which directly impart a permanent colour to textile fibres without previous treatment, and those which dye fibres only after these have been specially treated. The members of the first class are termed "substantive" dyestuffs ; those of the second are called "adjective" dyestuffs. The process by which textiles are treated in order to take up the adjective dyestuffs is known as "mordanting." This consists in impregnating the fibres with some metallic salt, such as aluminium acetate or an antimony salt in the presence of tannic acid ; on treating the impregnated textile with an adjective dyestuff, an insoluble metallic salt of the dye is precipitated in the interstices of the fibres. On the nature of the fibre depends largely whether a dyestuff is adjective or substantive ; many dyes are substantive to wool or silk, but adjective to cotton.

In the course of the text we have met with certain classes of compounds all of which are endowed with colour—of these the most important are the azo compounds, and substances containing the quinonoid groupings :

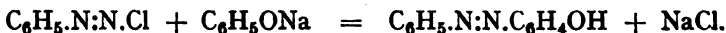


Now azobenzene and benzoquinone, whilst strongly coloured, are not dyestuffs, since they cannot be caused to adhere permanently to any fibres. In order that coloured compounds should possess this property, they must contain certain other groupings besides those which cause the substance to possess colour. The dyeing properties of an organic substance are

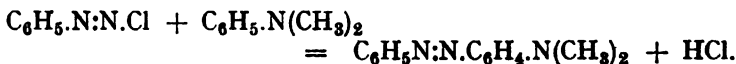
conditioned by two factors: (1) the presence in the molecule of a colour-bearing complex (such as the azo —N=N— grouping; (2) the presence of a salt-forming radicle (such as an amino or hydroxyl group). In a true dyestuff both of these conditions must be fulfilled, for only by means of a salt-forming radicle is the molecule enabled to affix itself to the fibre.

AZO DYES

Azo compounds containing salt-forming radicles are prepared by the general method of "coupling" a diazo compound with a suitable aromatic derivative. Thus on treating an alkaline solution of a phenol or naphthol with a salt of diazobenzene, a hydroxyazo compound is produced. In the case of phenol itself, the dyestuff *p*-hydroxyazobenzene is formed:

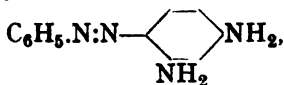


In the same way, the dyestuff *p*-dimethylaminoazobenzene is produced by the action of diazobenzene upon dimethylaniline:

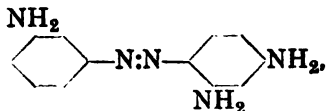


It will be recalled that *p*-aminoazobenzene (p. 382) is employed as a yellow dye, under the name of *aniline yellow*.

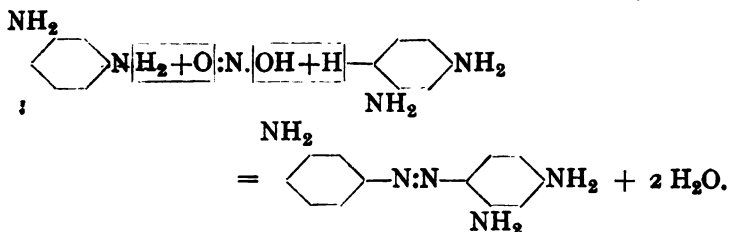
Dyes containing more than one amino group are known: such are *chrysoidin*:



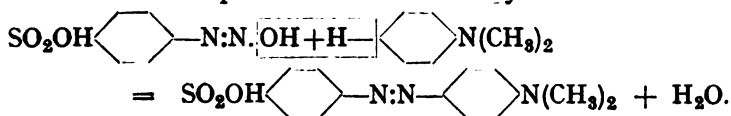
produced by coupling diazobenzene with *m*-phenylenediamine (p. 364), and *Bismarck brown*:



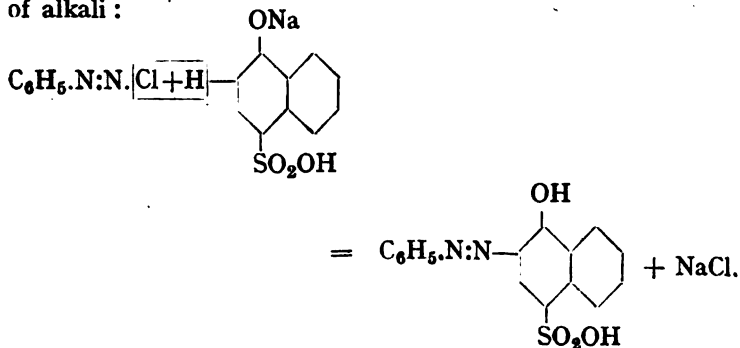
produced by the action of one molecular proportion of sodium nitrite upon two molecular proportions of *m*-phenylenediamine hydrochloride:



The hydroxyazo and aminoazo compounds thus prepared are as a rule insoluble in water, so that they must be employed in alcoholic solution for the dyeing of textiles. In order to avoid this disadvantage, sulphonated azo dyestuffs—containing the radicle $\text{—SO}_2\text{OH—}$ —are principally employed, since their sodium salts are soluble in water. For their preparation, either an aminosulphonic acid, such as sulphanilic acid (p. 369), may be diazotised and coupled with hydroxy or amino compound, or else a simpler diazo compound may be coupled with a hydroxy- or amino-sulphonic acid. An example of the first type of reaction is the preparation of *helianthin* (*methyl-orange*), from diazotised sulphanilic acid and dimethylaniline :



An example of the second method of preparation is the action of diazobenzene upon α -naphthol-4-sulphonic acid in presence of alkali :



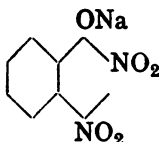
As will readily be understood, an almost endless series of such azo dyestuffs can be prepared by varying the reacting substances.

NITRO DYES

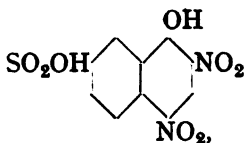
The nitro group is also capable of conferring colour upon many aromatic compounds in which it is a substituent. It will be recalled, for instance, that the nitrophenols are either themselves coloured, or form coloured salts.

1,2,4-Trinitrobenzene, a substance of light yellow colour, is not a dyestuff; 1,2,4-trinitrophenol (*picric acid*), on the other hand, dyes wool yellow. Here, as in the azo dyes, a salt-forming radicle (hydroxyl) is necessary as well as the colour-producing nitro groups.

Another example of a nitrophenol which can be employed as a dyestuff is *Martius's yellow*, which is the sodium salt of the 2,4-dinitro derivative of α -naphthol :



As this dyestuff, however, is but sparingly soluble in water, and possesses but slight affinity for fibres, it has been supplanted by its sulphonated derivative :



termed *naphthol yellow S*, in which these disadvantages have disappeared.

TRIPHENYLMETHANE DYES

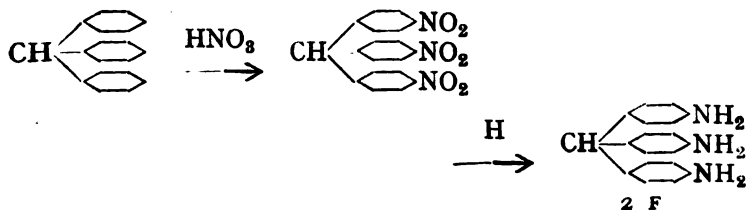
The series of dyestuffs which are derivatives of the aromatic hydrocarbon triphenylmethane (p. 325) are of especial interest,

since it is to this class that belong the first of the synthetic dyes prepared from coal tar.

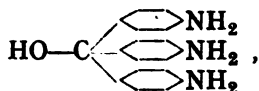
In 1856 Perkin, in the course of some experiments upon crude "aniline oil"—a mixture of aniline, *o*-toluidine, and *p*-toluidine, which was the purest form of aniline then obtainable—found that on oxidation it yielded a purple-coloured dyestuff. Other samples of aniline oil, differing somewhat in composition, were found to produce other dyestuffs, of which the chief in theoretical importance was a red dye called *pararosaniline*.

When aniline and the toluidines came to be readily procurable in the pure state, it was found that this dyestuff could be produced by the action of mild oxidising agents upon a mixture of two equivalents of aniline with one of *p*-toluidine; the product, pararosaniline, was found to possess the formula $C_{19}H_{19}ON_3$. A peculiarity of this substance is that it forms salts free of oxygen; the hydrochloride, for instance, has the composition $C_{19}H_{18}N_3Cl$, this indicating that a chlorine atom has replaced an oxygen atom and a hydrogen atom in the molecule; moreover, the free base is colourless, whilst the oxygen-free hydrochloride possesses an intense red colour.

When this red-coloured salt is reduced, it is converted into a colourless salt of a base of the composition $C_{19}H_{19}N_3$, which is an aromatic primary amine containing three $-NH_2$ groups, for all three nitrogen atoms may be removed by means of the diazo reaction. On replacing the amino groups by hydrogen, a hydrocarbon $C_{19}H_{16}$ is formed; this is identical with triphenylmethane. The colourless base $C_{19}H_{19}N_3$ may be synthesised from triphenylmethane by nitration (whereby nitro groups enter in the *para* position in each nucleus) and subsequent reduction:

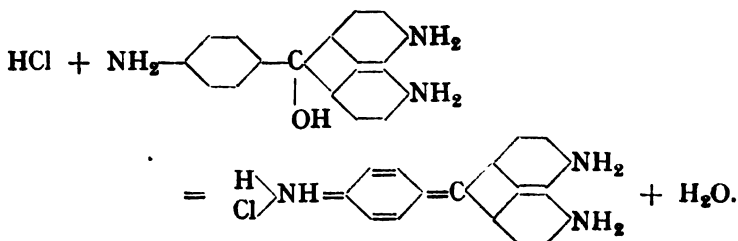


This base, *p.p.p-triaminotriphenylmethane*, on mild oxidation, is converted into the hydroxy derivative :

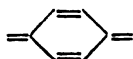


which is identical with the base of pararosaniline.

Now when this colourless hydroxy compound is treated with hydrochloric acid, some profound structural alteration must take place. It is necessary to assume this in order to account for the transition from a colourless base to a coloured salt, for the simple replacement of a hydroxyl group by a chlorine atom does not bring about so marked a physical change. The general consensus of opinion favours the view that one of the benzenoid nuclei becomes *quinonoid* (p. 346) on the addition of acid, this change being expressible by :



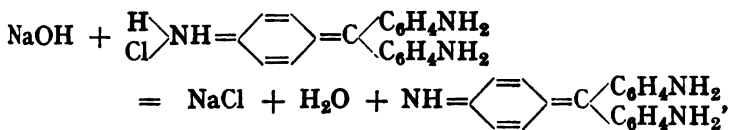
It has already been mentioned (p. 347) that all compounds containing this quinonoid grouping :



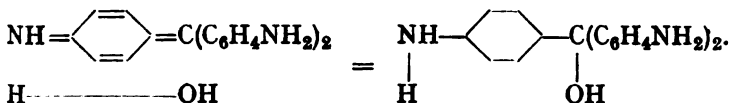
are endowed with colour ; and throughout the series of triphenylmethane dyes it is customary to ascribe to the coloured forms a quinonoid structure of this type. This formulation is supported, in the case of pararosaniline, by the fact that the chlorine atom behaves in every way as if it were attached to a nitrogen atom and not a carbon atom, as might be expected in the case of a derivative of triphenylcarbinol.

Perhaps the most convincing argument in support of the

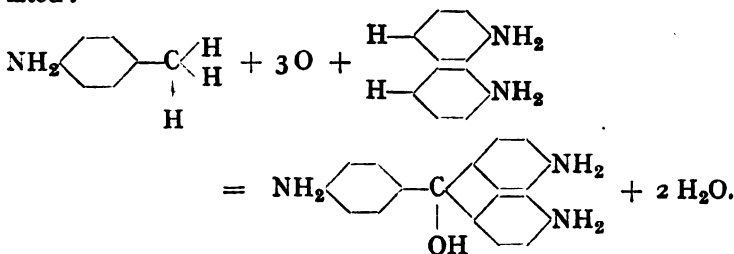
above view is that a coloured salt of pararosaniline, on treatment with alkali, yields a coloured, water-soluble base. This is none other than the quinonoid anhydride of pararosaniline :



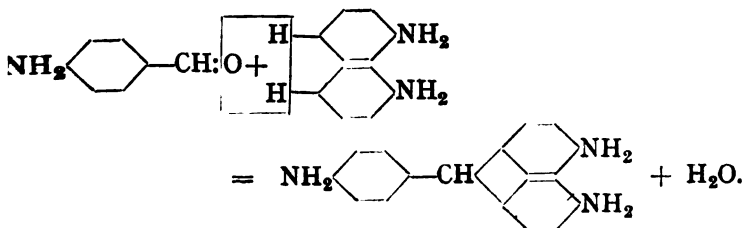
but it rapidly takes up water, passing spontaneously into the colourless, insoluble derivative of triphenyl carbinol :



The formation of pararosaniline from two molecular proportions of aniline and one of *p*-toluidine can thus be formulated :

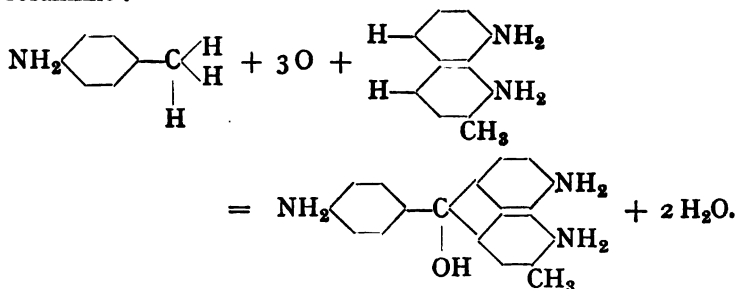


p.p.p-Triaminotriphenylmethane, the colourless base formed by the reduction of pararosaniline, may be synthesised by the condensation of one molecule of *p*-aminobenzaldehyde with two molecules of aniline :



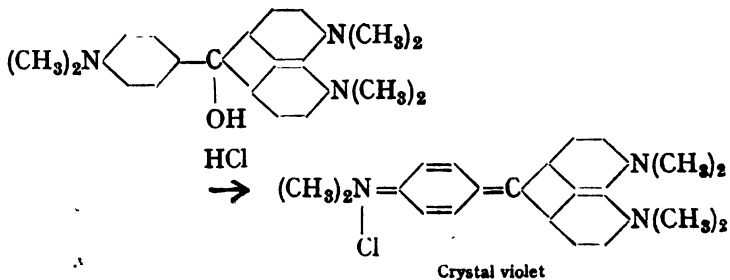
It is called the *leuco* base of pararosaniline, this expression being derived from λευκός (white). All triphenylmethane dyes, and many others, yield leuco compounds on reduction, these being derivatives of triphenylmethane $(C_6H_5)_3C.H$, the dyestuffs being anhydrous quinonoid salts derived from triphenylcarbinol $(C_6H_5)_3C.OH$.

Rosaniline, a dye of similar properties, prepared by the oxidation of a mixture of equal molecular proportions of aniline, *o*-toluidine and *p*-toluidine, is formed in the same way as pararosaniline :

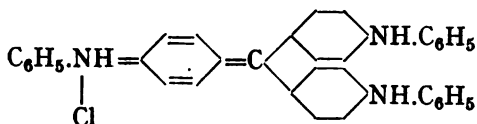


This dye was one of the first to be manufactured, being prepared by oxidation of the "aniline oil" consisting of a mixture of aniline with the *o*- and *p*-toluidines. Its hydrochloride is often known as *fuchsin*.

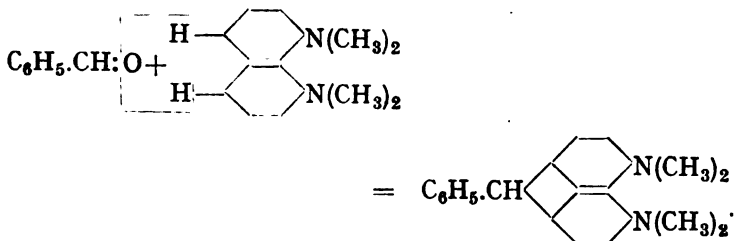
The nitrogen atoms in these dyestuffs may also exist in the secondary or tertiary conditions. Such is *crystal violet*, the hydrated base of which is the hexamethyl derivative of pararosaniline or hexamethyl-*p.p.p*-triamonotriphenylcarbinol :



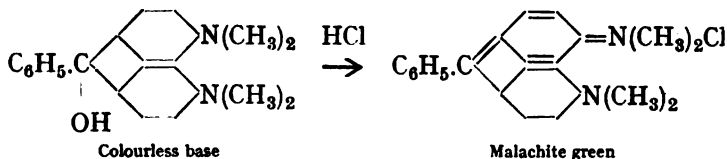
Diphenylamine blue is the hydrochloride of the triphenyl derivative of pararosaniline :



In *malachite green* one of the phenyl radicles is entirely unsubstituted. It will be recalled that its leuco base is formed by dehydration of a mixture of benzaldehyde and dimethylaniline (p. 367) :

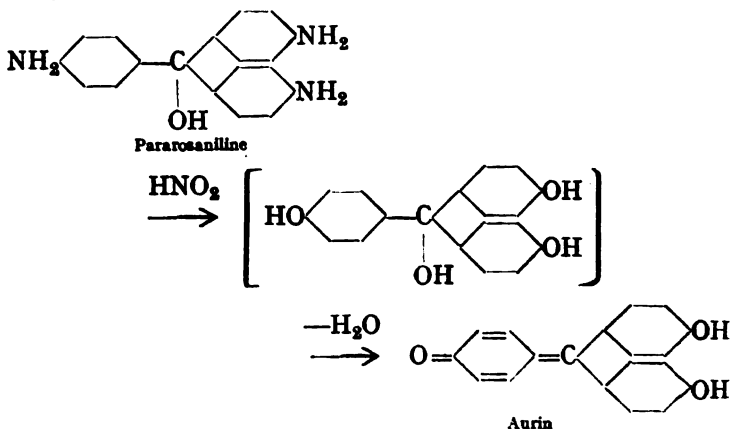


This leuco compound, on oxidation, passes into the hydrated base of malachite green :

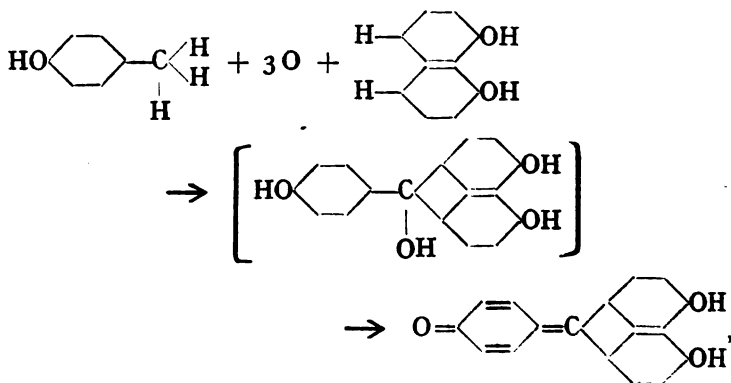


Analogous compounds of oxygen can also behave as dyestuffs. If, by means of the diazo reaction, the three amino groups in pararosaniline be replaced by hydroxyl groups, a dye named *aurin* or *pararosanolic acid* is formed. In this case, however, the free p.p.p-trihydroxytriphenylcarbinol is

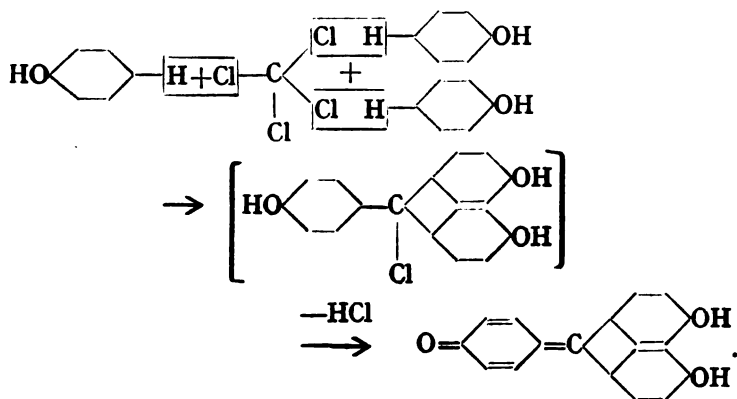
unstable and at once loses water to form the quinonoid anhydride :



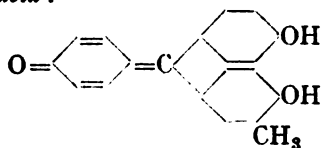
Aurin shows its ketonic character by forming a colourless addition-product with sodium hydrogen sulphite. It may be synthesised by the oxidation of a mixture of two molecules of phenol with one of *p*-cresol :



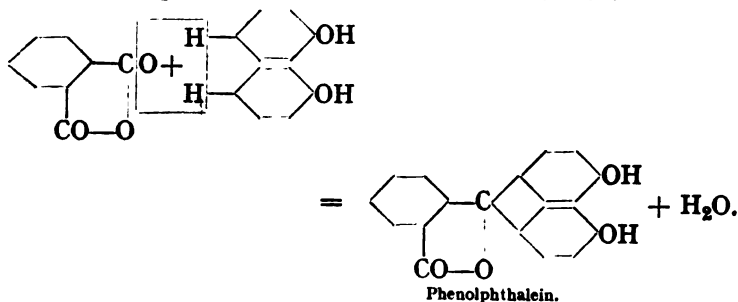
or by the action of carbon tetrachloride (in presence of zinc chloride or aluminium chloride) upon phenol :



The analogous compound corresponding to rosaniline is known as *rosolic acid* :

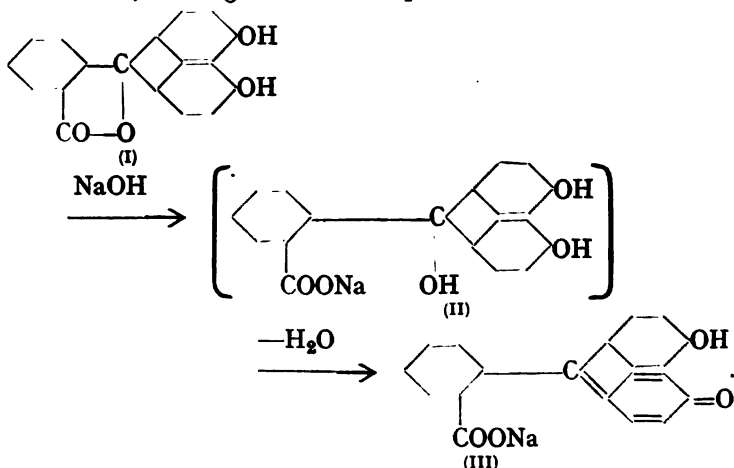


A group of coloured substances which are closely akin to the above are the **phthaleins**, which contain a carboxyl group. The simplest of these is *phenolphthalein*, prepared by the condensation of phenol with phthalic anhydride (p. 398).

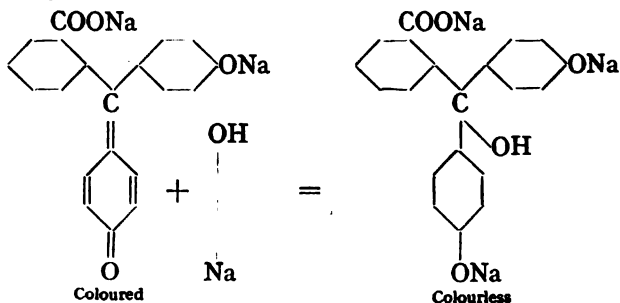


Phenolphthalein, which is colourless, is thus a lactone, or internal ester (I), and, like other esters, can be hydrolysed by means of alkali. This hydrolysis is readily effected, and

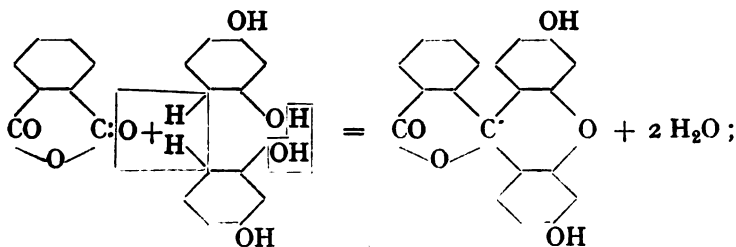
takes place instantly on addition of alkali, yielding a salt of dihydroxytriphenylcarbinolcarboxylic acid (II), which, like the trihydroxytriphenylcarbinol corresponding to aurin, at once loses water, forming the coloured quinonoid anhydride (III):



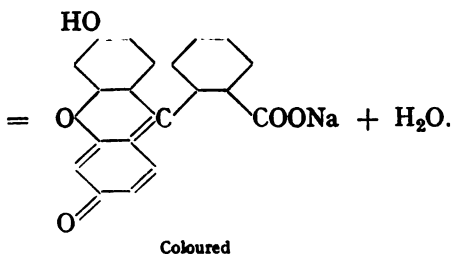
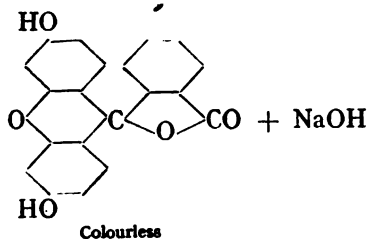
On addition of acid the reverse change instantly takes place, with regeneration of the colourless lactone. Hence phenolphthalein can be employed as an indicator. It is interesting to note that the red colour of phenolphthalein is destroyed by the addition of very concentrated alkali hydroxide; this is due to the fact that above a certain concentration of alkali the quinonoid portion of the molecule is converted into a salt-forming phenolic structure:



Phenolphthalein is not a true dyestuff; *fluorescein*, the phthalein prepared by the condensation of phthalic anhydride and resorcinol (p. 345), on the other hand, is a dye, and its sodium salt is employed under the name *uranin*. Fluorescein is both a lactone and an ether :

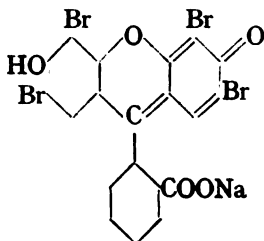


in general behaviour towards acids and alkalis it resembles phenolphthalein, yielding a coloured metallic salt of quinonoid structure on treatment with alkali :



Fluorescein is notable for the intense green fluorescence which it exhibits in alkaline solution.

Uranin is not largely employed as a dye, but its tetrabromo derivative, *eosin* :

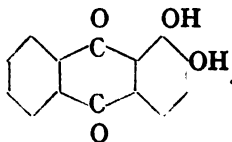


finds wide application as a dyestuff and as the colouring-matter in red ink.

QUINONE DYES

In the triphenylmethane dyestuffs the coloured properties are ascribable to a quinonoid structure which is present under certain conditions only. Dyestuffs are also known in which the quinonoid condition is, so to speak, *permanent*. It will be recalled that simple quinones are all endowed with colour; they are, however, not true dyestuffs, which fact may be explained by stating that the colour-producing complex is present, but no salt-forming group. It is therefore to be anticipated that if we can prepare a derivative of a quinone which contains suitable salt-forming groups, this substance will possess dyeing properties.

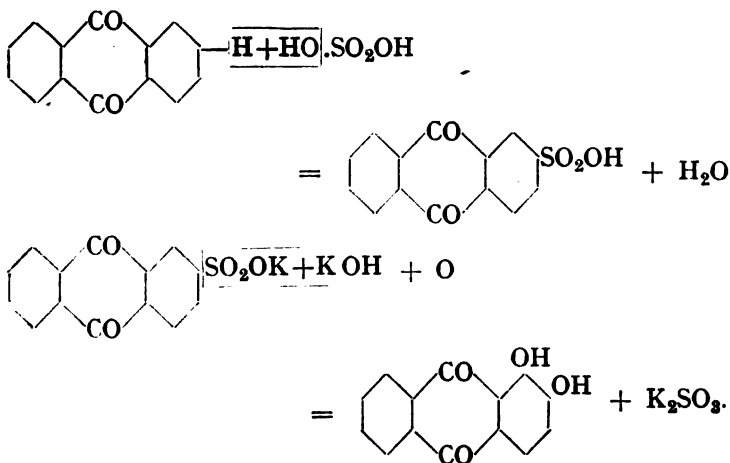
And this is indeed the case. The chief of such dyestuffs is a dihydroxy derivative of the coloured compound anthraquinone (p. 419), called *alizarin* :



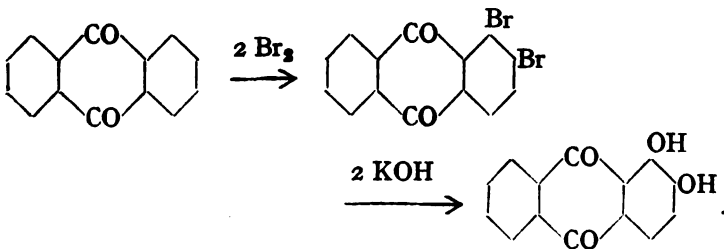
The use of alizarin as a red dyestuff is of great antiquity. It has long been known that the root of the madder plant (*Rubia*), which contains alizarin, can be employed, in a crushed condition, for dyeing mordanted fabrics red. Until recent years the only source of this dyestuff was the madder plant,

which was cultivated extensively for this purpose ; but since the time when its synthetical production was shown to be a commercial possibility, the madder industry has declined into practical non-existence.

Alizarin may be synthesised in a variety of ways. It is technically produced from anthraquinone (prepared by oxidation of the anthracene obtained from coal-tar) by heating this to 160° with fuming sulphuric acid, and subsequently fusing the resulting sulphonic acid with alkali in presence of some oxidising agent such as potassium chlorate :

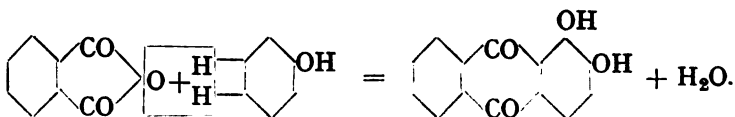


The original method of synthesis, devised in 1869 by Graebe and Liebermann, consisted in brominating anthraquinone and fusing the resulting dibromoanthraquinone with alkali :

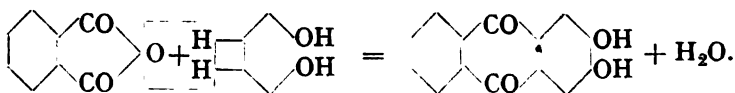


By this synthesis a naturally occurring dyestuff was for the first time prepared artificially.

A synthesis which at the time threw light upon the constitution of alizarin was effected by heating a mixture of phthalic anhydride and catechol with concentrated sulphuric acid :



The isomeric dyestuff *hystazarin* is simultaneously produced :



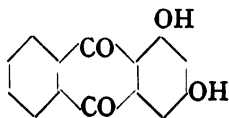
Alizarin, being a phenol, forms metallic salts. It dissolves in aqueous alkali ; on adding such a solution to a solution of a salt of a metal of the alkaline earth or aluminium series, insoluble salts, termed *lakes*, are precipitated ; these lakes are employed as pigments. It is by the formation of such salts that alizarin affixes itself to the fibre, which must be mordanted with a suitable metallic acetate. The colour of alizarin lakes varies with the metal :—those prepared from salts of calcium, strontium, barium, or aluminium are red, the ferric salt is violet, whilst the chromic salt is brown.

The calcium lake is employed in order to isolate the alizarin from the alkaline fused mass in its technical production ; on treating this salt with hydrochloric acid, the free alizarin is precipitated and placed on the market in the form of a wet paste. Dry alizarin may be sublimed, and can thus be obtained in the form of needles, often several inches in length.

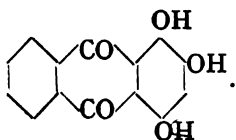
The alizarin in the madder root is present in the form of a species of glucoside, called *ruberythric acid*, which behaves as a weak monobasic acid and must therefore contain one hydroxyl group. On hydrolysis this substance yields one molecular

proportion of alizarin and two of glucose, so that the glucose residues are probably combined, as in amygdalin (p. 388), in the form of a disaccharide such as maltose.

In addition to alizarin, other dyes of the alizarin family are present. The chief of these are *purpuroxanthin*



and *purpurin*

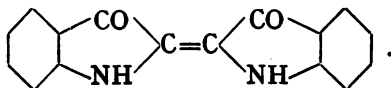


INDIGO

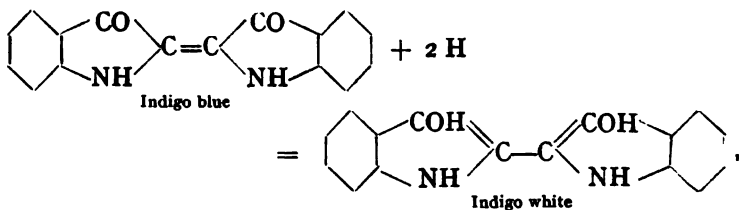
The history of indigo closely resembles that of alizarin. It is a blue dyestuff obtained from certain plants, particularly the *Indigofera*. Its employment as a blue dye is of considerable antiquity, having been practised by the ancient Britons, who coloured their bodies blue by the aid of the woad (*Isatis*) plant, which contains indigo. Indigo is a mixture of different substances, the chief of which is *indigo blue* or *indigotin*: this can be isolated from crude indigo by sublimation.

Indigotin is present in the indigo plant—like alizarin in madder—in combination with a sugar; this glucosidic compound is called *indican*.

Indigotin is a blue crystalline solid with a reddish metallic lustre, and is insoluble in water, in alcohol, in dilute acids, and in dilute alkalis. The structural formula for indigotin is

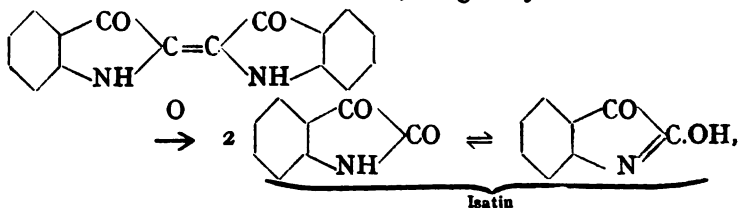


Like the triphenylmethane dyes, indigotin yields a leuco compound on reduction; this is *indigo white*:

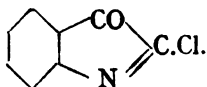


a colourless substance which resembles a phenol in forming metallic salts, whereby it is capable of entering into solution in dilute alkalis. Advantage of this fact is taken in dyeing with indigo: the textile to be dyed is soaked in such a solution, and then exposed to the air, whereby oxidation takes place, indigotin being deposited upon the fibres.

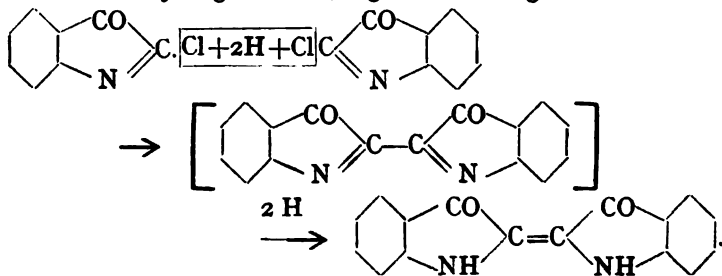
When oxidised with nitric acid, indigotin yields *isatin*:



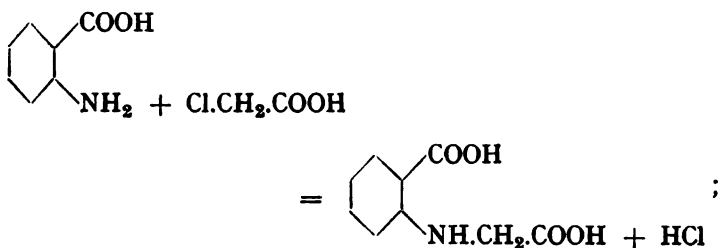
which, on treatment with phosphorus pentachloride, yields *isatin chloride*:



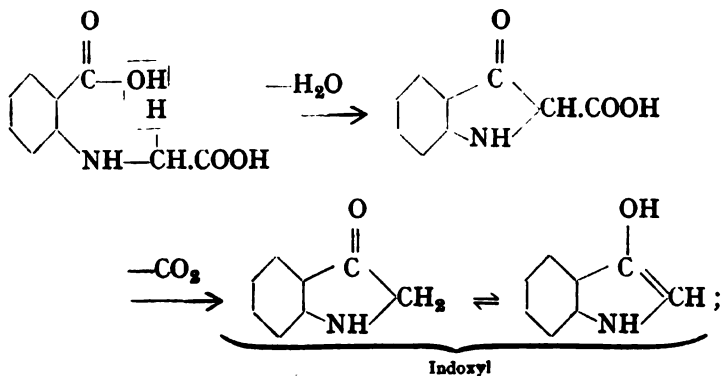
This, on reduction in glacial acetic acid solution by means of zinc dust or hydrogen iodide, regenerates indigotin:



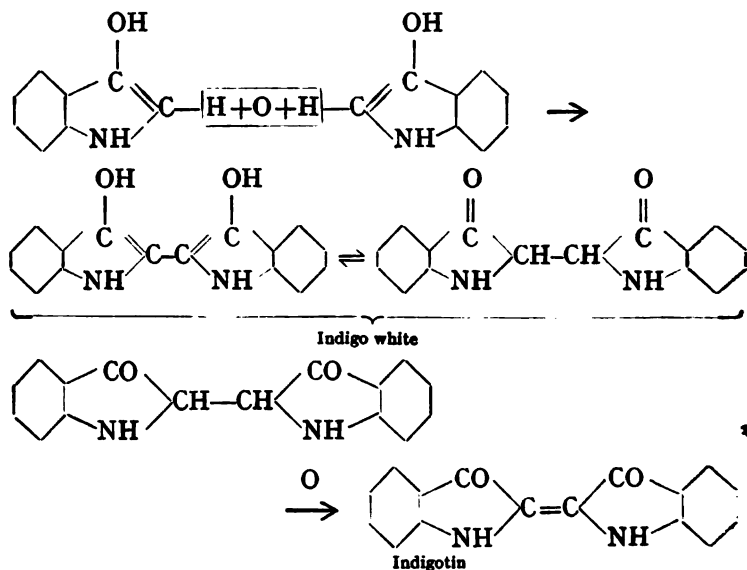
Like the growing of madder, the cultivation of the indigo plant, which was formerly an industry of considerable dimensions in India, has of recent years greatly diminished, owing to the more profitable synthetical methods of producing the dye. Of these the following is the chief: anthranilic acid (p. 404), on treatment with chloroacetic acid, yields a derivative of glycine (p. 289) called phenylglycine-*o*-carboxylic acid:



this, on fusion with alkali, yields *indoxyl*, which is at once converted into indogotin, the reaction taking place in the following stages:



the indoxyl then undergoes oxidation by the action of air in the presence of the hot alkali, yielding indigo white, which at once loses two further atoms of hydrogen :



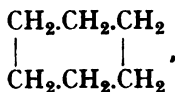
CHAPTER XXXVII

ALICYCLIC AND HETEROCYCLIC COMPOUNDS

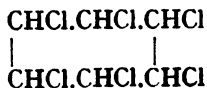
IN the earlier chapters, dealing with aliphatic compounds, reference was made to certain substances of cyclic structure, in which the ring was composed of atoms of carbon and some other element, such as oxygen or nitrogen. Some of these were mentioned (p. 300) in the chapter dealing with the chemical status of benzene and its derivatives, and it was shown how aromatic compounds differ from these, two of the chief points of difference in benzene being that the ring is composed exclusively of carbon atoms, and that a peculiar type of unsaturation prevails.

ALICYCLIC COMPOUNDS

A series of cyclic compounds is known, in which the ring is made up entirely of carbon atoms, but in which the valencies of these atoms are disposed as in the aliphatic compounds. These are the *alicyclic* compounds, this word "alicyclic" being formed by elision from the words "aliphatic" and "cyclic." The existence of two of these substances has already been mentioned : *hexahydrobenzene*

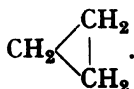


and *benzene hexachloride*

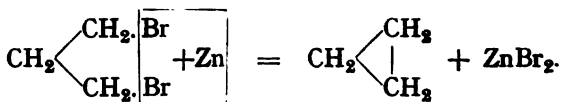


(p. 305). Both of these substances are typical alicyclic compounds.

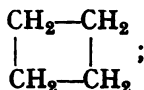
The first member of the series of alicyclic hydrocarbons is **cyclopropane** (or *trimethylene*)



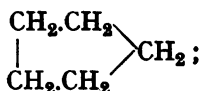
This is formed by the action of zinc upon trimethylene bromide (α,γ -dibromopropane, p. 104) :



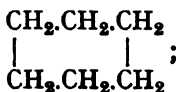
Subsequent members are **cyclobutane** (*tetramethylene*)



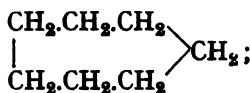
cyclopentane (*pentamethylene*)



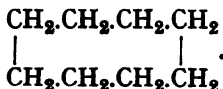
cyclohexane (*hexamethylene*, *hexahydrobenzene*)



cycloheptane (*heptamethylene*)

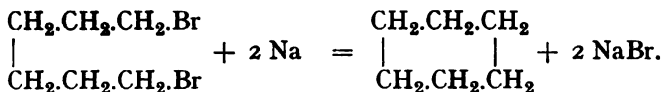


and **cyclooctane** (*octamethylene*)



These are all hydrocarbons which yield derivatives analogous to the open-chain aliphatic compounds derived from the paraffins.

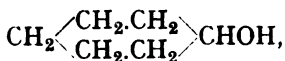
Chief in importance is cyclohexane, which, as stated on p. 304, can be produced by the action of sodium upon α,ζ -di bromohexane :



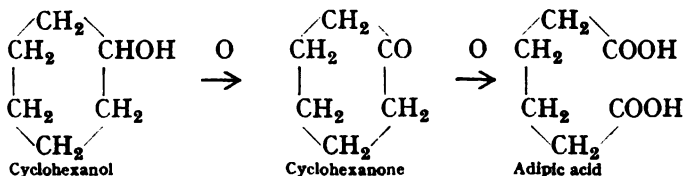
It is more readily obtained by passing the vapour of benzene together with hydrogen over finely-divided nickel at 200° . This method of hydrogenation, devised by Sabatier and Senderens, is applicable to a large number of derivatives of benzene. Another method of hydrogenation consists in treating benzene under pressure with hydrogen in presence of finely-divided platinum. In both cases the metal acts as a catalyst.

Cyclohexane melts at 5° and boils at 80° , and behaves in every way like a paraffin hydrocarbon, except in the one particular, mentioned on p. 304, that on heating under pressure with finely-divided platinum alone, it loses six atoms of hydrogen, yielding benzene.

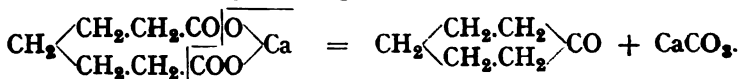
The monohydroxy derivative, *cyclohexanol* or *hexahydrophenol*



which is produced by passing a mixture of hydrogen and the vapour of phenol over finely-divided nickel at 220° , is a typical secondary alcohol. It melts at 25° and boils at 160° . On oxidation it yields the corresponding ketone, *cyclohexanone*, which on further oxidation yields the open-chain dicarboxylic acid adipic acid :

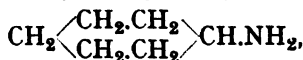


Cyclohexanone can also be produced by heating the calcium salt of the dicarboxylic acid pimelic acid :



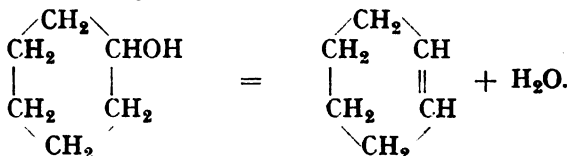
It is a typical ketone, reacting with sodium hydrogen sulphite, hydrogen cyanide, hydroxylamine, and phenylhydrazine. It boils at 154° .

Aniline, on treatment with hydrogen in presence of finely-divided nickel at 180° , yields *cyclohexylamine* :

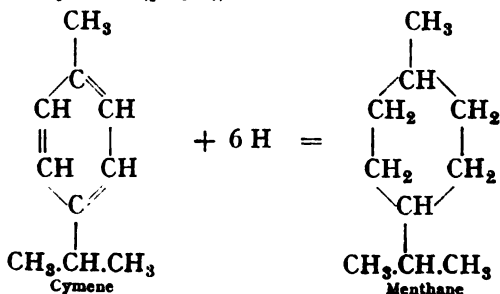


a strongly basic liquid boiling at 134° , which behaves strictly as an aliphatic primary amine.

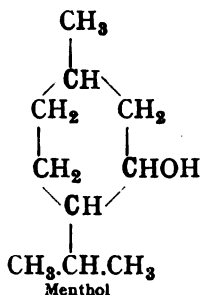
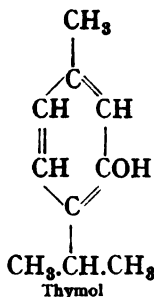
Cyclohexanol, on dehydration, yields an unsaturated cyclic hydrocarbon, *cyclohexene*, which possesses all the properties of a derivative of ethylene :



Many substances containing the cyclohexane ring occur in nature ; these are, however, derived not from cyclohexane itself, but from one of its homologues, *menthane* (1-methyl-4-isopropylcyclohexane), which may be prepared by the hydrogenation of *cymene* (p. 324) :

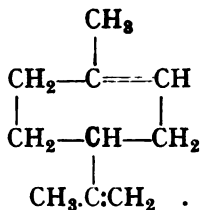


Menthane itself has not been found in nature, but one of its hydroxy derivatives is *menthol*, the chief constituent and odorous principle of oil of peppermint. This is a hexahydro derivative of thymol (p. 342) :



Menthol obtained from peppermint is optically active ; examination of the formula will show the presence in the molecule of three asymmetric carbon atoms (heavy type). A mixture of menthol with its stereoisomers is formed by the catalytic hydrogenation of thymol. On oxidation it is converted into the corresponding ketone *menthone*, which is also present in oil of peppermint.

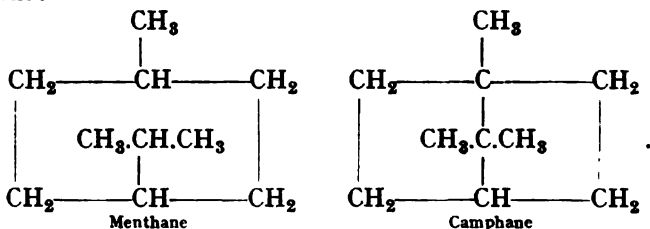
Another derivative of menthane is *limonene*, the principal constituent of oil of lemon, which is an unsaturated hydrocarbon containing the cyclohexene system :



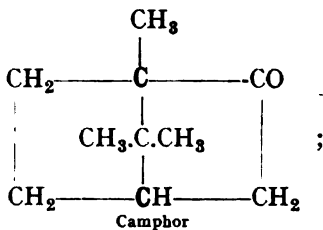
It is optically active ; both *dextro* and *laevo* varieties are found in nature, as is also the inactive variety, *dipentene*, consisting of an equimolecular mixture of the two optical antipodes.

Camphane is a hydrocarbon allied to menthane ; in this compound the central carbon atom in the isopropyl

structure of the menthane molecule connects the 1 and 4 carbon atoms in the cyclohexane ring, resulting in a *dicyclic* system :

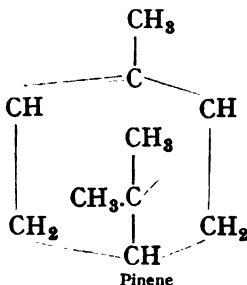


The ketone *camphor* is closely related in structure to this hydrocarbon :



it is optically active, containing two asymmetric carbon atoms.

Finally, in the dicyclic hydrocarbon *pinene*, the chief constituent of oil of turpentine, the 2 and 4 carbon atoms in the cyclohexane ring are bridged by the isopropylidene structure :



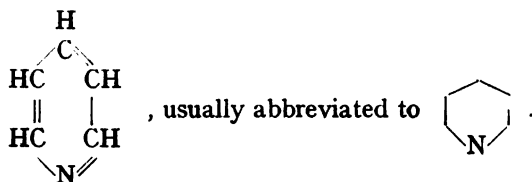
These closely-allied and numerous families of naturally-occurring substances, of which a few important examples have

above been mentioned, are all grouped together into one class, and are generally designated as the *terpenes*.

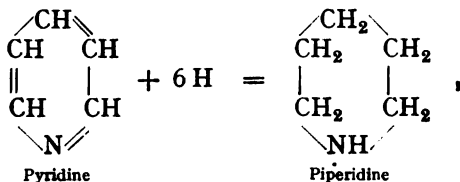
HETEROCYCLIC COMPOUNDS

Strictly speaking, this term includes all cyclic compounds in which the ring system is composed of members consisting of atoms of more than one element. But it is rather to a class of heterocyclic compounds of which the members display certain analogies with the aromatic series that we shall here principally devote our attention.

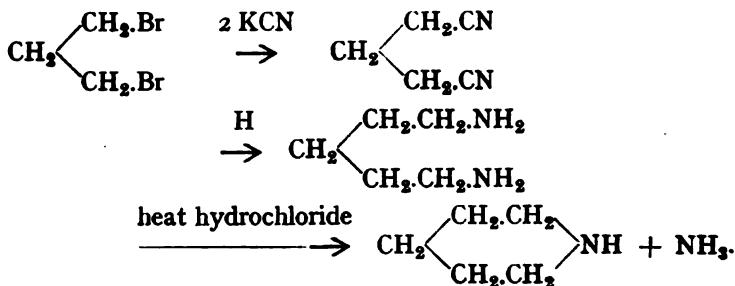
One of the most important of these substances is *pyridine*, a base of empirical formula C_5H_5N , which occurs in small quantity in coal-tar, and forms a larger proportion of the oil obtained by the dry distillation of bones. It is a colourless liquid, of characteristic odour, which boils at 115° and is miscible with water. In chemical constitution it may be regarded as benzene in which one of the methenyl groups $\geq CH$ is replaced by a tervalent nitrogen atom $\geq N$:



This constitution has been proved by the following steps:—pyridine can be hydrogenated by treatment in boiling alcoholic solution with sodium, yielding a secondary amine called *piperidine*:

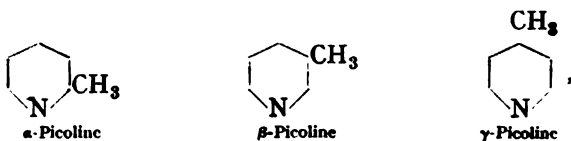


which is also formed by the following series of reactions :

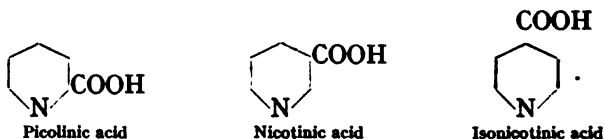


In accordance with its constitution as a tertiary amine, pyridine forms salts with acids, is unchanged by the action of acylating agents, and unites with alkyl halides to form quaternary ammonium salts.

Pyridine, like aniline, yields three series of monosubstitution-products, designated α , β , and γ . Examples of these are the three methylpyridines, or *picolines* :



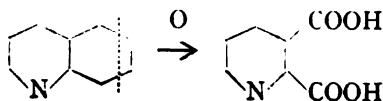
which on oxidation yield the corresponding pyridine-carboxylic acids :



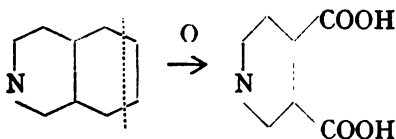
Derivatives of pyridine analogous to naphthalene are known. These are *quinoline* and *isoquinoline*, both of which are found in coal tar :



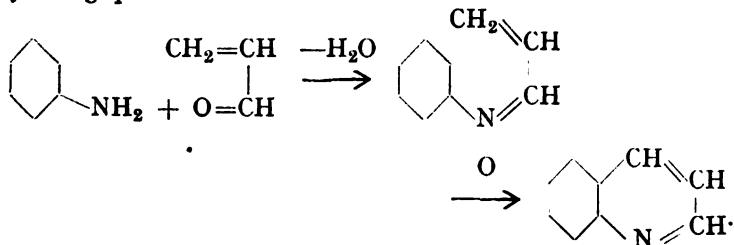
Quinoline, on oxidation, yields pyridine- α,β -dicarboxylic acid :



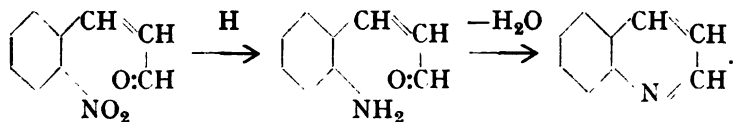
isoquinoline yields pyridine- β,γ -dicarboxylic acid :



The synthesis of quinoline, first effected by Skraup, consists of heating a mixture of aniline, glycerol, and sulphuric acid with an oxidising agent such as nitrobenzene or arsenic acid. The glycerol is first dehydrated to acrolein (p. 150) ; this combines with the aniline to form an anil (p. 369), which is then oxidised, yielding quinoline :

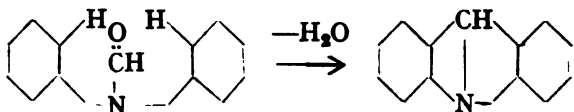


A simpler synthesis was subsequently devised by Baeyer, who obtained quinoline by the action of a reducing agent upon *o*-nitrocinnamic aldehyde :

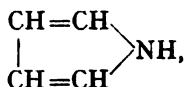


An analogue of anthracene containing the pyridine system

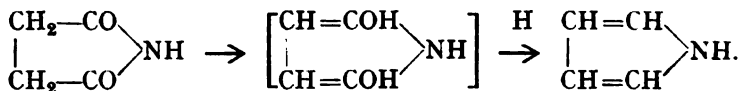
is *acridine*, which is found in coal-tar and may be synthesised by heating formyldiphenylamine with zinc chloride :



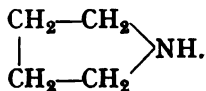
Another constituent of bone-oil is *pyrrole*, which also possesses an aromatic character. Pyrrole is a five-membered cyclic compound of the formula



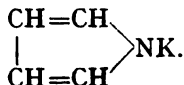
which is formed by heating succinimide with zinc dust :



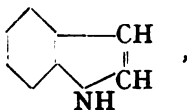
It is a colourless liquid, boiling at 134° , the vapour of which develops a red colour upon a pine shaving moistened with hydrochloric acid. Pyrrole can, with great difficulty, be hydrogenated, yielding the strongly basic substance *pyrrolidine*



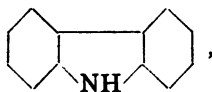
A striking feature of pyrrole is the weakness of its basic character, for it is more weakly basic than even aniline. It resembles succinimide in being able to form metallic derivatives, such as potassium pyrrole



The pyrrole nucleus can exist in a condensed form with the benzene nucleus ; the analogue of naphthalene is *indole*

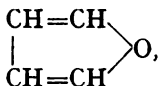


which is related to indoxyl and isatin (pp. 446, 447); the analogue of anthracene is *carbazole*

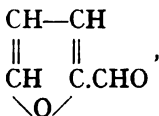


which occurs in coal-tar (p. 418). Both of these substances form potassium derivatives on heating with solid potassium hydroxide.

Analogous to pyrrole is *furfurane* (or *furane*)



the aldehydic derivative of which, *furfural* (*furaldehyde*, or *furfurol*)



is produced by heating pentoses (p. 272) with concentrated hydrochloric acid. This aldehyde displays a striking similarity to benzaldehyde.



is a liquid boiling at 84° which occurs in coal-tar, and cannot be separated from benzene by fractional distillation. Of all the heterocyclic compounds above mentioned it exhibits the greatest analogy with benzene, yielding an extensive series of parallel derivatives, the general properties of which are closely similar. It can be synthesised by heating a mixture of sodium succinate and phosphorus trisulphide.

SUMMARY

In the following pages the chief reactions of the principal classes of compounds are briefly recapitulated, by the aid, when necessary, of chemical equations. Only simple types—that is to say, the reactions of compounds containing one salient class of radicle—are discussed. Thus, for example, hydroxylic compounds and carboxylic acids are dealt with as individual classes, but hydroxy-acids find no mention.

HYDROCARBONS

Hydrocarbons are insoluble in, and of lower specific gravity than, water. They readily burn in air, yielding water and carbon dioxide ; those containing less than five atoms of hydrogen in proportion to two atoms of carbon in the molecule burn with smoky flames (liberation of unoxidised elemental carbon).

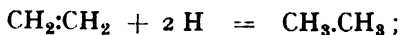
Paraffins (Saturated hydrocarbons).

(1) Are not attacked at ordinary temperatures by any acids or alkalis. Sodium and potassium are without effect. Oxidation takes place extremely slowly on heating to a high temperature with powerful oxidising agents.

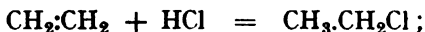
(2) They react with chlorine and bromine in sunlight, yielding halogen substitution-products and hydrogen halides. Iodine is without action.

Olefines (Ethylenic hydrocarbons).

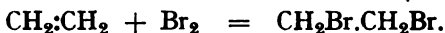
(1) They combine with nascent hydrogen, yielding paraffins :



with hydrogen halides, yielding alkyl halides :



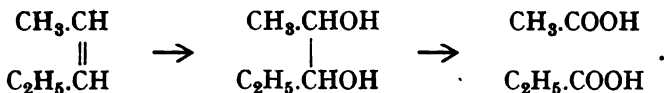
and with halogens, yielding alkylene halides :



With concentrated sulphuric acid they yield alkylsulphuric acids (alkyl hydrogen sulphates) :

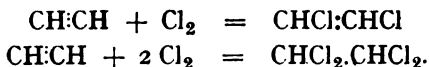


(2) With oxidising agents they yield firstly glycols, then carboxylic acids containing fewer carbon atoms :



Acetylenes.

(1) They combine with either two or four atomic proportions of nascent hydrogen, or either one or two molecular proportions of hydrogen halide or halogen, yielding respectively ethylenic and saturated compounds :



(2) They take up the elements of water on treatment with an acid solution of mercuric chloride, yielding carbonyl compounds :

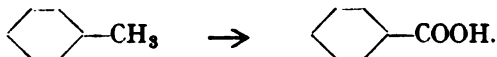


(3) Those in which a hydrogen atom is attached to a triply-bound carbon atom (*i.e.* containing the grouping $-\text{C}\equiv\text{C}.\text{H}$) yield metallic derivatives such as : $-\text{C}\equiv\text{C}.\text{Na}$, $-\text{C}\equiv\text{C}.\text{Ag}$.

Aromatic hydrocarbons.

(1) May be nitrated, chlorinated, brominated, etc.

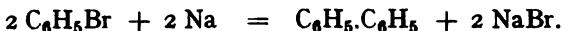
(2) Those containing extranuclear carbon atoms yield carboxylic acids on oxidation :



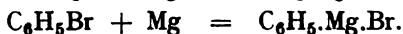
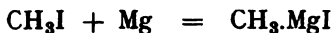
HALOGENATED HYDROCARBONS

They are insoluble in water. As a general rule, aryl halides, and alkyl halides containing bromine, iodine, and more than one atom of chlorine, are heavier than water.

The halogen atom is eliminated from all classes of halogen compound by the action of such metals as sodium, higher hydrocarbons being formed :



On treatment in dry ethereal solution with magnesium, Grignard's reagents are formed :



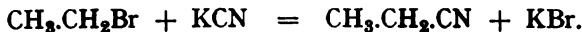
The reactions of Grignard's reagents are summarised on p. 235.

Aliphatic series.

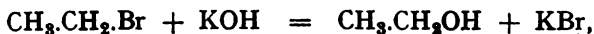
(1) Alkyl halides combine with ammonia and with amines :



(2) They react with many metallic salts, replacing the metal by alkyl radicles :



(3) On heating with *aqueous* alkalis they yield alcohols :



but yield ethers and ethylenes on boiling with *alcoholic* alkalis :



(4) Saturated hydrocarbons are formed by the action of nascent hydrogen :



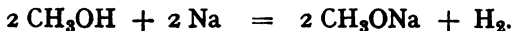
Iodine compounds are the most reactive, chlorine compounds the least.

Aromatic series.

The halogen atom is eliminated only by the agency of certain metals, such as sodium or magnesium. Ammonia and alkalies are without action.

HYDROXYLIC COMPOUNDS

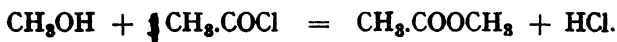
All hydroxylic compounds react with sodium, with displacement of hydrogen by the metal :



On treatment with phosphorus halides, a halogen atom takes the place of the hydroxyl group :

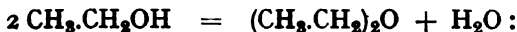


On treatment with acid chlorides, or with acids themselves under suitable conditions, esters are formed :



Alcohols.

(1) On gentle catalytic dehydration they yield ethers :



on more powerful dehydration they yield (with the exception of methyl alcohol) ethylenic hydrocarbons :



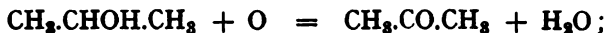
Secondary alcohols yield olefines more readily than primary alcohols, tertiary alcohols do so more readily than secondary alcohols.

(2) On oxidation :—

Primary alcohols yield aldehydes :



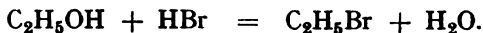
secondary alcohols yield ketones :



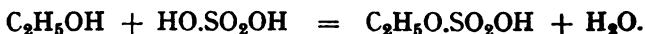
tertiary alcohols yield ketones containing fewer carbon atoms in the molecule :



(3) On heating with hydrogen halides they yield alkyl halides :



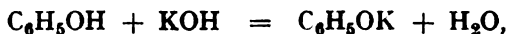
(4) On warming with concentrated sulphuric acid they yield alkylsulphuric acids :



When excess of alcohol is present, ethers are formed ; when excess of sulphuric acid is present, olefines are produced.

Phenols.

(1) They possess weakly acid properties, forming salts which are stable in aqueous solution :



but are decomposed by carbonic acid :



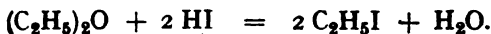
(2) Many phenols develop characteristic colours with dilute ferric chloride.

ETHERS

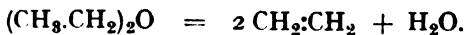
Are insoluble in water. They are unchanged by the action of sodium and of alkalies, are not attacked by dilute mineral acids in the cold. They dissolve unchanged in cold concentrated sulphuric acid.

Aliphatic.

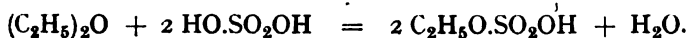
(1) On heating with concentrated hydriodic acid they yield alkyl iodides :



(2) On powerful catalytic dehydration they yield olefines :



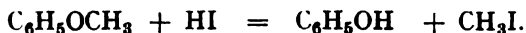
(3) On gently warming their solutions in concentrated sulphuric acid, they yield alkylsulphuric acids :



On strongly heating such solutions, olefines are formed.

Aromatic (alkyl ethers of phenols).

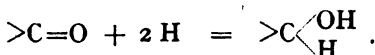
(1) On heating with concentrated hydriodic acid, they yield phenols and alkyl iodides :



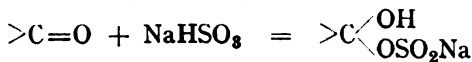
(2) On warming with aluminium chloride they yield phenols and alkyl chlorides.

CARBONYL COMPOUNDS

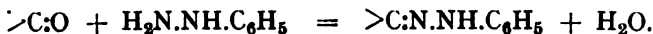
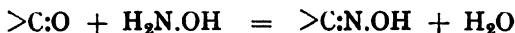
(1) They yield alcohols on reduction :



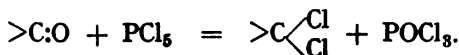
They also form addition-products with sodium hydrogen sulphite and with hydrogen cyanide :



(2) On treatment with hydroxylamine, phenylhydrazine, and certain other $-NH_2$ compounds, condensation takes place :



(3) With phosphorus pentachloride, dichloro compounds are formed :

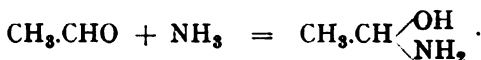


Aldehydes.

- (1) On reduction, they yield *primary* alcohols.
 (2) They are easily oxidised to carboxylic acids :

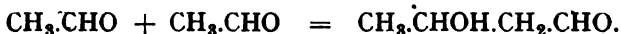


- (3) With ammonia, they form addition or condensation-products, such as :

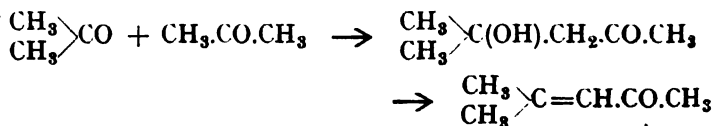


- (4) On addition of a small quantity of sulphuric acid, some aldehydes polymerise.

- (5) In presence of a small quantity of alkali, many aliphatic aldehydes undergo the aldol-condensation :

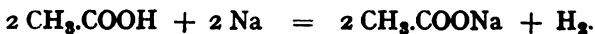
**Ketones.**

- (1) On reduction, *secondary* alcohols are formed.
 (2) Oxidation takes place with difficulty, with disruption of the molecule.
 (3) In presence of alkali, some ketones undergo the aldol-condensation, yielding products which readily lose water, being thereby converted into unsaturated compounds :

**CARBOXYLIC ACIDS**

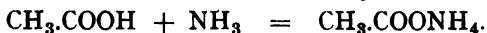
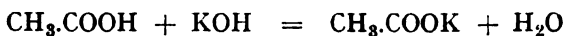
They are weaker acids than the majority of inorganic acids, but form stable salts with bases. They resist the action of all but the most powerful oxidising and reducing agents.

- (1) They react with sodium and the more electropositive metals, yielding hydrogen and metallic salts :

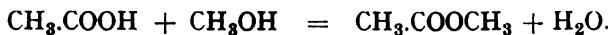


- (2) Salts are also formed by the action of carboxylic

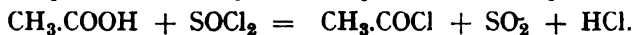
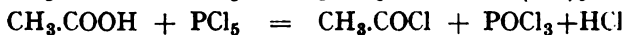
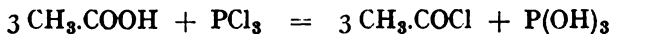
acids upon many metallic hydroxides and upon ammonia or amines :



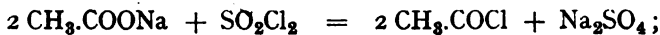
(3) On heating carboxylic acids with alcohols, esters are produced, this reaction being aided by the presence of dry hydrogen chloride or concentrated sulphuric acid :



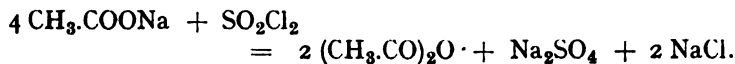
(4) On treatment with phosphorus trichloride, phosphorus pentachloride, or thionyl chloride, carboxylic acids are converted into acid chlorides :



(5) On treating salts of carboxylic acids with excess of sulphuryl chloride, acid chlorides are produced :



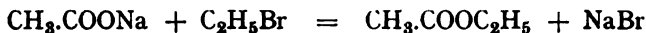
when, however, the salt is in excess, acid anhydrides are formed :



(6) Acid anhydrides are also produced by the action of acid halides upon carboxylic acids :



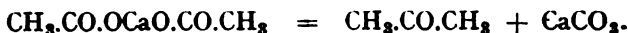
(7) On treating salts of carboxylic acids with alkyl halides, esters are formed :



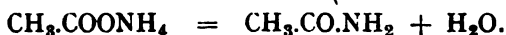
(8) Salts of carboxylic acids break down on heating with soda-lime, yielding hydrocarbons :



(9) Calcium salts of carboxylic acids yield carbonyl compounds on heating :



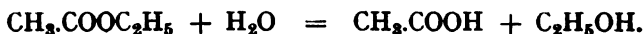
(10) Ammonium salts of carboxylic acids, on heating to a high temperature, yield simple amides :



CARBOXYLIC ESTERS

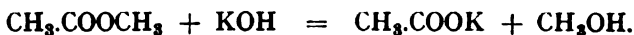
They are generally insoluble in and lighter than water, and are neutral to indicators.

(1) On prolonged heating with water they yield the corresponding carboxylic acids and alcohols :

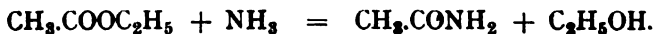


This hydrolysis takes place more readily in presence of dilute mineral acids.

(2) On boiling with aqueous or alcoholic alkalies, salts and alcohols are formed :

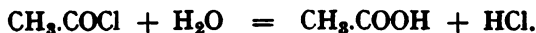


(3) Many esters are decomposed by aqueous ammonia, yielding acid amides :



ACID HALIDES

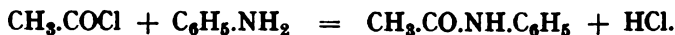
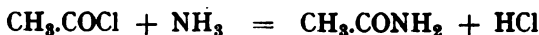
(1) They are decomposed by water, yielding hydrogen halides and carboxylic acids :



(2) They react with alcohols and phenols, yielding hydrogen halides and esters :



(3) They react with ammonia, primary amines, and secondary amines, yielding simple or substituted amides :



(4) On heating with dry metallic salts of carboxylic acids, they yield acid anhydrides :



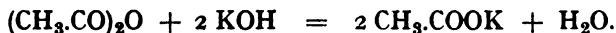
ACID ANHYDRIDES

They are insoluble in water.

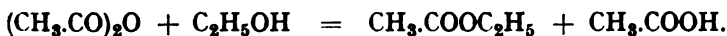
(1) They are hydrolysed on prolonged boiling with water :



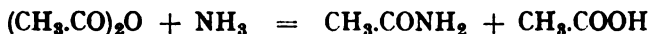
and more rapidly with alkalis :



(2) On boiling with alcohols they yield esters :



(3) With ammonia and primary and secondary amines, they form simple and substituted amides :



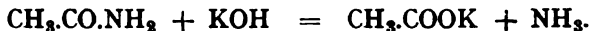
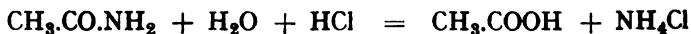
AMIDES

They are neutral substances, as a rule solid at ordinary temperatures.

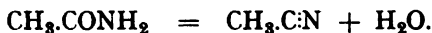
(1) They are hydrolysed by prolonged heating with water, yielding ammonium salts :



(2) On boiling with acids or alkalies, hydrolysis takes place more rapidly :



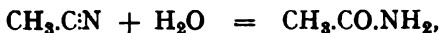
(3) Simple amides are dehydrated by heating with phosphorus pentoxide, phosphorus pentachloride, or thionyl chloride, yielding nitriles :



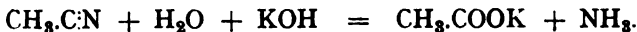
NITRILES

They are neutral substances, insoluble in water. Many of them are liquids.

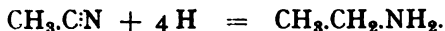
(1) On gentle hydrolysis by means of dilute acids or alkalies they yield amides :



which can undergo further hydrolysis, so that on treatment with powerful hydrolytic reagents, such as concentrated hydrochloric acid or potassium hydroxide, carboxylic acids are produced :



(2) On reduction they are converted into primary amines :



AMINES

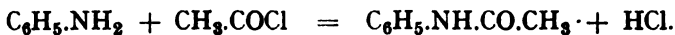
All types of amines, with rare exceptions, are bases which form with acids salts of the type of ammonium chloride. These salts are decomposed by alkalies, the free amines being regenerated.

Primary amines.

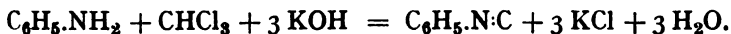
(1) On treatment with alkyl halides, salts of secondary amines are formed :



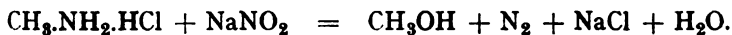
(2) Acylating agents convert primary amines into mono-substituted amides :



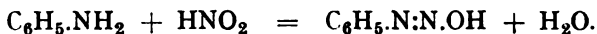
(3) On warming with a mixture of chloroform and alcoholic potash, evil-smelling isocyanides are formed :



(4) *Aliphatic* primary amines are instantly decomposed by nitrous acid, yielding alcohols with evolution of nitrogen :



(5) *Aromatic* primary amines, on treatment with nitrous acid, are converted into diazo compounds :



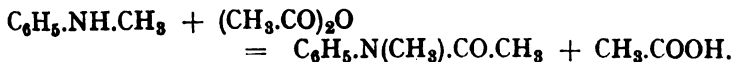
A summary of the reactions of diazo compounds can be found on p. 376.

Secondary amines.

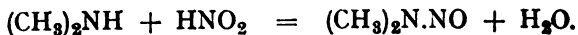
(1) On treatment with alkyl halides, salts of tertiary amines are formed :



(2) With acylating agents, disubstituted amides are produced :

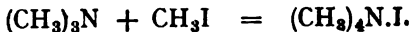


(3) By the action of nitrous acid, secondary amines yield nitrosoamines :



Tertiary amines.

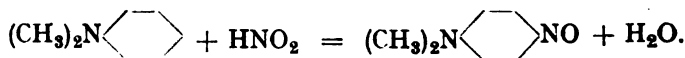
(1) They yield quaternary ammonium salts by the action of alkyl halides :



(2) They are unaffected by acylating reagents.

(3) *Aliphatic* tertiary amines are unchanged on treatment with nitrous acid.

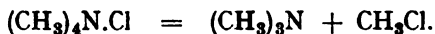
(4) Many *aromatic* tertiary amines yield *p*-nitroso derivatives by the action of nitrous acid :



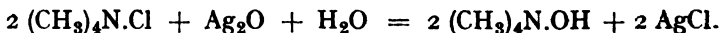
Quaternary ammonium salts.

Are salts of strong bases, and are not decomposed by alkalis.

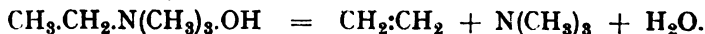
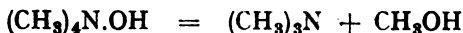
(1) On strongly heating, quaternary ammonium halides break down into tertiary amines and alkyl halides :



(2) On treating in aqueous solution with silver oxide, the halides yield the strongly basic quaternary ammonium hydroxides :

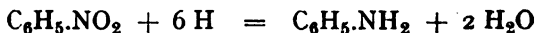
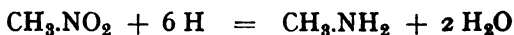


(3) Quaternary ammonium hydroxides, on heating alone, break down into tertiary amines, yielding, when possible, ethylenic compounds :

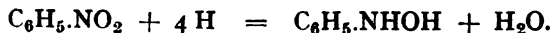


NITRO COMPOUNDS

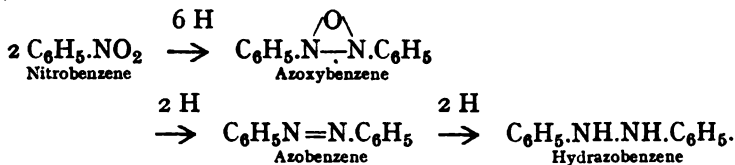
(1) Aliphatic and aromatic nitro compounds yield primary amines on reduction in acid solution :



(2) On reduction in neutral solution, aromatic nitro compounds are converted into aryl derivatives of hydroxylamine :



(3) On reduction in alkaline solution, aromatic nitro compounds yield a series of reduction-products, according to the conditions :



PROBLEMS

1. A pure substance, in which only carbon, hydrogen, and nitrogen have been detected, was submitted to quantitative analysis: 0.1340 gram of substance gave 0.1998 gram of CO_2 and 0.1023 gram of H_2O ; 0.0982 gram of substance gave 20.4 cc. of moist nitrogen, measured under barometric pressure 755 mm. at 18° (vapour-pressure of water at 18° is 15.36 mm.). Calculate the simplest empirical formula for the compound.

2. An organic acid, containing only carbon, hydrogen, and oxygen, yielded the following data:—0.1173 gram gave 0.1954 gram of CO_2 and 0.0640 gram of H_2O ; 0.1248 gram, on titration, neutralised 18.9 cc. of N/10 alkali. Calculate the simplest empirical formula for the acid, indicating the proportion of acidic hydrogen atoms in the molecule.

3. The vapour-density of a hydrocarbon, found on analysis to contain 92.30 per cent. of carbon and 7.70 per cent. of hydrogen, was determined by Victor Meyer's method:—0.1061 gram of substance were volatilised, and 25.0 cc. of moist air, measured under 750 mm. pressure at 17° (vapour-pressure of water at 17° is 14.42 mm.), were collected. What is the true empirical formula for the hydrocarbon?

4. A substance, in which only carbon, hydrogen, sulphur, and chlorine have been detected, was submitted to analysis:—0.1450 gram gave 0.2169 gram of CO_2 and 0.0372 gram of H_2O ; 0.1756 gram gave 0.1427 gram of AgCl ; 0.1632 gram gave 0.2159 gram of BaSO_4 . The molecular weight was estimated by the freezing-point method:—0.1947 gram of substance in 19.30 grams of benzene (the depression-constant of which is 50), lowered the freezing-point by 0.285° . Calculate the true empirical formula for the substance.

5. An acid belonging to the formic acid series was titrated with normal sodium hydroxide solution:—1.76 gram required 20.0 cc. Calculate the molecular weight of the acid. What

substances would be produced by heating the acid with excess of sodium hydroxide? (*Univ. Coll., London, 1909.*)

6. An acid contains only carbon, hydrogen, and oxygen. On combustion it gave 47.7 per cent. of carbon and 5.08 per cent. of hydrogen. The silver salt contains 65.0 per cent. of silver. The free acid, on heating, gives carbon dioxide and another acid. What is the probable composition of the acid and of the acid produced by heating it? (*Univ. Coll., London, 1913.*)

7. What volume of oxygen at 0°C . and 760 mm. will be required to burn completely one litre of a gaseous hydrocarbon whose formula is C_xH_{2x} , and what volume of carbon dioxide will be formed? How would you determine the value of x ? (*Queen's Univ., Belfast; Inter. Sci., 1911.*)

8. An organic compound has a vapour-density of 118. On combustion, 0.3933 gram of the substance yielded 0.4400 gram of CO_2 and 0.0600 gram of H_2O . The substance contains only carbon, hydrogen, and bromine. Calculate its formula and state how you would determine which of the probable isomers it was. (*Queen's Univ., Belfast, B.Sc.Hons., 1911.*)

9. Write the structural formulæ for two ethers whose true empirical formula is $\text{C}_4\text{H}_{10}\text{O}$, and state how each of the ethers may be prepared. (*Queen's Univ., Belfast, Inter. Sci., 1911.*)

10. A compound A has the following percentage composition :—
C = 55.8 per cent., H = 8.5 per cent., N = 10.9 per cent., O = 24.8 per cent.; when it is treated with dilute acid it gives ammonia and a compound B of composition C = 55.4 per cent., H = 7.7 per cent., O = 36.9 per cent. Compound B, when boiled with caustic soda solution, is decomposed into carbon dioxide, alcohol, and a compound C of composition C = 62.1 per cent., H = 10.3 per cent., O = 27.6 per cent. How might these reactions be expressed by means of graphic formulæ? (*Univ. Coll., London, 1909.*)

11. A substance A has the formula $\text{C}_2\text{H}_5\text{O}_2\text{N}$. With caustic potash it forms a body $\text{C}_2\text{H}_4\text{O}_2\text{NK}$. With hydrochloric acid, a compound $\text{C}_2\text{H}_6\text{O}_2\text{NCl}$ is produced from A. Nitrous acid with A yields a substance $\text{C}_2\text{H}_4\text{O}_3$. With acetyl chloride and A, the reaction-product is $\text{C}_4\text{H}_7\text{O}_3\text{N}$. Heated with baryta, A decomposes, yielding carbon dioxide and methylamine. What is the structure of the compound A? (*Queen's Univ., Belfast, B.Sc.Hons., 1912.*)

12. A substance A has the formula $(\text{CH}_2\text{Br})_n$. On treatment

with potassium cyanide it yields a body which on hydrolysis produces a compound B having the general formula $(C_3H_5O_2)_n$. B easily gives an internal anhydride. On bromination, B yields a substance having the formula $C_4H_5O_4Br$, which, on treatment with potash, gives fumaric acid. What is A, and how would you prepare it? (*Queen's Univ., Belfast, B.Sc.Pass, 1912.*)

13. A substance of composition C = 43.94 per cent., H = 4.27 per cent., N = 8.52 per cent., Cl = 43.29 per cent., yields an immediate precipitate of silver chloride when treated with silver nitrate solution:—0.287 gram require 17.5 cc. of N/10 $AgNO_3$. On treatment in hot aqueous solution with sodium nitrite, it yields nitrogen and a compound which possesses slightly acidic properties; the vapour-density of this second compound is 64. To which classes of compounds could you assign these two substances?

14. Compare the properties of the following compounds: $CH_3CH_2NH_2$, $CH_3CO.NH_2$, $NH_2CO.NH_2$; giving your answers in tabular form. (*Univ. Coll., London, 1910.*)

15. Enumerate briefly the various reactions where sulphuric acid is used for producing organic compounds. (*Univ. Coll., London, 1908.*)

16. Given methyl alcohol, and employing no other organic compounds, how would you proceed to synthesise betaine?

17. Given benzene, how would you prepare from it salicylaldehydophenylhydrazone?

18. Suggest a synthetical method of preparing glycerol.

INDEX

- ACETALDEHYDE**, 30, 44, 140, **148**
Acetals, 146
Acetamide, 38, **174**
Acetanilide, 360, 361, **868**
Acetic acid, 30, 36, **163**
 anhydride, 36, **172**
Acetoacetic ester, **259**, 339
Acetone, 38, 44, 140, **152**, 317
Acetonitrile, 174, **221**
Acetophenone, 389
Acetyl-anthranilic acid, 405
 chloride, 37, **170**
 methylaniline, 365, 368
 phenylhydrazine, 379
 salicylic acid, 401
Acetylene, 18, 77, 86, 87, 88, **89**, 317
Acid amides, 173
 anhydrides, 171, 393
 chlorides, 159, 169
Aconitic acid, 257
Acridine, 458
Acrolein, 133, **150**
Acrylic acid, 168
Adipic acid, 318, 451
Alanine, 291
Alanyl-alanine, 292
Albumins (*see* **PROTEINS**).
Alcohols, 20, 106
Aldol, 150, **151**
Alizarin, 421, **442**
Alkoxides, 20, 34, 338
Alkyl carbonates, 179
 chloroformates, 179
 halides, 94
 magnesium halides, 97, 111,
 139, 159, **235**, 392
 orthocarbonates, 179
 sulphates, 197
 sulphonates, 215, 333
 sulphuric acids, 193
Allene, 85
Allyl alcohol, **126**, 150
 disulphide, 212
 halides, 99
 isothiocyanate, 227
 sulphide, 212
Allylene, 89, 317
Amines, 21, 198, 358
Amino-acetic acid, 289
 azobenzene, **882**, 430
 benzoic acids, 404
 phenols, **371**, 426
Amygdalin, 388
Amygdalinic acid, 388
Amyl alcohols, 118
 nitrite, 195
Anethole, 387
Aniline, 314, 356, **360**, 424, 426
Anils, 361, **369**, 383
Anisaldehyde, 387
Anisic acid, 402
Anisole, 343
Anthracene, 319, 410, **417**
Anthranilic acid, 399, **404**
Anthranol, 421
Anthraquinol, 421
Anthraquinone, 410, **419**, 420,
 443
Arabinose, 271
Arabitol, 134
Arbutin, 389
Arginine, 294
Arsines, 239
Aspartic acid, 294
Asymmetry, 123
Aurin, 437
Azo compounds, 377, 381
 dyes, 430
Azobenzene, 356, **381**
Azoxybenzene, 356, **380**

- BAEYER, 457
 Beckmann, 69
 Benzal-aniline, 361, **369**, 385
 acetone, 386
 chloride, **331**, 384, 396
 malonic acid, 396
 Benzaldehyde, 384
 cyanohydrin, 385, 388
 phenylhydrazone, 385
 Benzaldoxime, 385
 Benzamide, 394
 Benzanilide, 394
 Benzene, 301, 317, **320**
 hexachloride, 305, 422, 449
 sulphochloride, 334
 sulphonamide, 334
 sulphonic acid, 313, 321, **332**
 Benzhydrol, 390
 Benzhidine, 383
 Benzoic acid, 313, 321, 386, **391**
 anhydride, 393
 Benzoin, 386
 Benzonitrile, 394
 Benzophenone, 325, 389, **390**
 Benzotrichloride, 331, 392
 Benzoyl-aminoacetic acid, 394
 benzoic acid, 420
 chloride, 387, **393**
 Benzoylation, 393
 Benzyl alcohol, 342, **386**
 chloride, **331**, 396
 cyanide, 396
 Benzylamine, **364**, 395
 Benzylidene- (*see* BENZAL-).
 Berthelot, 75
 Betaine, 291
 Bismarck Brown, 430
 Bismuthines, 240
 Biuret, 180
 reaction, 295
 Boiling-point, 50
 Bromination, 327
 Bromo-acetophenone, 389
 benzene, 321, **328**
 nitrobenzenes, 428
 Butanes, 11, 76
 Butyl alcohols, 117
 Butyric acid, 165
 Camphane, 453
 Camphor, 454
 Cane-sugar, 281
 Carbamates, 181
 Carbamide, **179**, 182
 Carbazole, 459
 Carbon disulphide, 183
 oxysulphide, 183
 suboxide, 188
 tetrabromide, 103
 tetrachloride, 8, **102**
 Carbonyl (group), 24, 141
 chloride, 102, **178**
 Carboxyl (group), 25, 157
 Carbylamines, 201, **229**
 Carius, 60
 Catechol, 344
 Cellulose, 285
 Chloral, 101, **151**
 Chlorination, 327, 423
 Chloro-acetanilides, 362
 acetophenone, 389
 acetyl chloride, 160, 172
 anilines, 362
 benzene, 305, **328**
 benzoic acids, 330, 403
 formic esters, 179
 naphthalenes, 412
 nitrobenzenes, 352
 toluenes, 330
 Chloroanil, 348, 362
 Chloroform, 8, **101**
 Chrysoidin, 430
 Cinnamaldehyde, 368
 Cinnamic acid, 396
 Cis-trans isomerism, 267
 Citric acid, 256
 Coal-tar, 319, 411, 418
 Combustion, 54
 Condensation, 29
 Configuration, 255
 Cresols, 342
 Crotonaldehyde, 151
 Crum-Brown rule, 315, 424
 Cryoscope, 71
 Crystal Violet, 436
 Crystallisation, 51
 Cyamelide, 224
 Cyanamide, 230
 Cyanates, 223
 Cyanic acid, 224
 Cyanides, 216

CACODYL, 239
 Caffein, 298

Cyanogen, 184, 187, 221

halides, 223

Cyanuric acid, 224

Cyclo-butane, 450

heptane, 450

hexane, 304, 449, 451

hexanol, 318, 451

hexanone, 451

hexene, 452

hexylamine, 452

octane, 450

pentane, 450

propane, 450

Cymene, 324, 452

Cystine, 295

DEHYDRATION, 29

Desmotropy, 261

Dextrins, 284

Dextrose (*see* GLUCOSE).

Diacetone-alcohol, 153, 154

Diacetyl, 155

Diastase, 116

Diazoaminobenzene, 378

Diazobenzene, 359, 373

perbromide, 377

Diazonium salts, 374

Diazotisation, 374

Dibenzalacetone, 386

Dibromobenzene, 329

Dichloroacetyl chloride, 160

Dichlorobenzenes, 328

Diglycyl-glycine, 293

Dihydro-anthracene, 418, 419

anthrone, 421

naphthalene, 411

Dihydroxyacetone, 133

Dimethylamine, 204

Dimethylaminoazobenzene, 430

Dimethylaniline, 366

Dinitro-benzene, 351

benzoic acid, 403

naphthalene, 413

naphthol, 432

phenol, 354

Dipentene, 453

Diphenic acid, 409

Diphenyl, 325, 376, 406

ether, 343

sulphide, 336, 375

Diphenylamine, 365

Blue, 437

Diphenylene, 406

Diphenylhydrazine, 383

Diphenylmethane, 325

Diphenylnitrosoamine, 366

Dipropargyl, 305

Disaccharides, 279

Disalicylide, 401

Distillation, 49

Disulphides, 210, 335

Dulcitol, 134

Dumas, Nitrogen estimation, 57

Vapour-density, 67

Dynamite, 194

EBULLIOSCOPE, 69

Emulsin, 388

Enzymes, 114, 388

Eosin, 442

Epichlorohydrin, 132

Erythritol, 134

Esterification, 29, 175

Esters, 32, 174

Ethane, 3, 76, 77, 79

Ethers, 21, 135, 343

Ethyl alcohol, 29, 114

benzoate, 392

bromide, 96, 98

chloride, 7, 98

ether, 32, 45, 135, 138

hydrosulphide, 210

iodide, 98

malonate, 188

mercaptan, 210

methyl ketone, 155

nitrate, 194

nitrite, 195

oxalate, 186

oxamate, 186

phthalate, 398

sulphate, 197

sulphide, 212

sulphone, 214

sulphuric acid, 195

Ethylamine, 205

Ethylene, 16, 32, 77, 83

chlorohydrin, 128

diamine, 205

glycol, 127

halides, 47, 100, 104

oxide, 129

Ethylidene halides, 100, 103

- FATS**, 130, 166
 Fehling's solution, 272, 276, 279, 281, 378
 Fermentation, 114, 165, 243, 256, 280, 281
 Ferricyanides, 218
 Ferrocyanides, 218
 Fischer, 274, 293, 298
 Fittig reaction, 321, 323, 327
 Fluorescein, 345, 398, 441
 Formaldehyde, 24, 147
 Formaldehydol, 147
 Formamide, 174
 Formic acid, 25, 161
 Friedel-Crafts reaction, 322, 324, 389, 390
 Fructose, 278, 285
 Fruit sugar (*see* **FRUCTOSE**).
 Fuchsin, 436
 Fumaric acid, 249, 265
 Furfural, 272, 459
 Furfurane, 459
 Furfurol (*see* **FURFURAL**).
 Fusel oil, 115
- GALACTONIC ACID**, 277
 Galactose, 277
 Gallic acid, 348, 402
 Gluconic acid, 275
 Glucosazone, 380
 Glucose, 114, 275, 285, 379, 388
 Glucosides, 276, 279, 388, 389, 444
 Glutamic acid, 299
 Glyceric acid, 133, 247
 Glycerol, 130
 chlorohydrins, 131, 132
 Glyceryl trinitrate, 132, 194
 Glycine, 289, 394
 anhydride, 292
 Glycocol (*see* **GLYCINE**).
 Glycogen, 285
 Glycol, 127
 Glycolide, 242
 Glycollic acid, 241
 Glycyl-glycine, 292
 Glyoxylic acid, 258
 Grape-sugar (*see* **GLUCOSE**).
 Grignard's reagents, 97, 111, 139, 159, 235, 327, 392
 Guaiacol, 344, 388
 Guanidine, 182, 230
 Guanin, 298
- HELIANTHIN**, 431
 Helicin, 389
 Hemihedrism, 251
 Heptamethylene, 450
 Hexachloroethane, 11
 Hexahydro-benzene, 304, 449, 451
 phenol, 451
 Hexamethylene, 450
 Hexamethylenetetramine, 148
 Hexoses, 272, 274, 278
 Hippuric acid, 290, 391, 394
 Hofmann reaction, 394, 399
 vapour density, 68
 Homology, 11
 Hydracrylic acid, 246
 Hydrazobenzene, 356, 383
 Hydrazones (*see* **PHENYLHYDRAZONES**).
 Hydrobenzamide, 385
 Hydrocinnamic acid, 397
 Hydrocyanic acid, 219
 Hydroquinone, 245, 389
 Hydroxy-azobenzene, 430
 benzaldehydes, 387, 427
 benzoic acids, 400, 401, 402, 427
 butyric acid, 247
 valeric acid, 248
 Hystazarin, 444
- IMIDE-CHLORIDES**, 221
 Iminoethers, 221
 Indican, 445
 Indigo, 445
 white, 445
 Indigotin, 445
 Indole, 459
 Indoxyl, 447
 Inulin, 285
 Invert sugar, 281
 Iodine number, 169
 Iodobenzene, 329
 dichloride, 329
 Iodoform, 103
 Iodonium bases, 329
 Iodosobenzene, 329
 Iodoxybenzene, 329
 Isatin, 445
 Isoamyl alcohol, 118
 nitrite, 195
 Isobutyl alcohol, 117
 Isobutyric acid, 166
 Isocyanates, 228

Isocyanides, 201, **229**
 Isomerism, 9
 Isonicotinic acid, 456
 Isophthalic acid, 323, **399**
 Isopropyl alcohol, 117
 iodide, 99
 Isoquinoline, 456
 Isothiocyanates, 227
 Isovalerianic acid, 118

KEKULÉ, 302, 307
 Keten, 36, 40, **172**
 Kjeldahl, 59
 Koerner, 309
 Kolbe reaction, 400, 402, 427

LACTASE, 281
 Lactic acid, 243
 Lactide, 244
 Lactones, 246, 398
 Lactose, 281
 Lactulose (*see* FRUCTOSE).
 Leucine, 291
 Leuco compounds, 436, 437, 445
 Limonene, 453
 Lysine, 294

MALACHITE GREEN, 368, **437**
 Maleic acid, 265
 anhydride, 249, **265**
 Malic acid, 247
 Malonic acid, 187
 Maltase, 388
 Maltose, 280
 Mandelic acid, 388, **403**
 Mandelonitrile, 385, 388, 389
 Mannitol, **184**, 277
 Mannonic acid, 277
 Mannosaccharic acid, 277
 Mannose, 277
 Martius's Yellow, 432
 Melibiose, 283
 Melting-point, 51
 Mentane, 452
 Menthol, 453
 Menthone, 453
 Mercaptans, 23, 209, 335
 Mercury alkyls, 237
 Mesidine, 425

Mesityl oxide, 154
 Mesitylene, 154, 317, **323**
 Mesotartaric acid, 254
 Methane, 2, 75, 76, **78**
 Methoxybenzoic acids, 401, 402
 Methyl alcohol, 20, **118**
 benzoate, 392
 bromide, 98
 chloride, 5, 6, **98**
 ether, 138
 ethyl ketone, 155
 glucoside, 276
 hydrosulphide, 210
 iodide, 98
 nitrate, 194
 nitrite, 195
 Orange, 431
 oxalate, 113, **186**
 picrate, 355, 372
 salicylate, 401
 sulphate, 197
 sulphide, 211
 sulphone, 214
 Methylacetanilide, 365, 368
 Methylacetylene, 89, 317
 Methylamines, 22, 198, **204**
 Methylaniline, **265**, 424, 425
 Methylidiphenylamine, 368
 Methylene chloride, 8, **102**
 Methyl-naphthalenes, 417
 Methylphenylhydrazine, 380
 Methylsalicylic acid, 401
 Methylsulphuric acid, 195
 Meyer, Vapour-density, 65
 Michler's ketone, 367
 Milk sugar (*see* LACTOSE).
 Monomethylaniline, 365
 Monosaccharides, 271
 Mucic acid, 277
 Murexide test, 299
 Mustard oil, 227

NAPHTHALENE, 319, 406, **411**
 dichloride, 412
 sulphonic acids, 413
 tetrachloride, 412
 Naphthaquinones, 416, **417**
 Naphthionic acid, 416
 Naphthoic acids, 417
 Naphthol, 414
 Yellow, 432

- Naphthylamines, 415
 Nicotinic acid, 456
 Nitration, 320, 350, 427
 Nitriles, 157, 173, **219**, 394
 Nitro-acetanilides, 363, 371
 acetophenone, 390
 anilines, 363, **370**
 benzaldehyde, 387, 397
 benzene, 313, **350**
 benzoic acids, 352, 403
 cellulose, 287
 chlorobenzene, 352
 cinnamic acids, 397
 ethane, 207
 glycerine, 132, 194
 methane, 207
 naphthalenes, 413
 phenols, 341, **353**, 427
 toluenes, 321, **351**
 Nitroso-amines, 365, 380
 benzene, 356, **357**, 381
 dimethylaniline, 367
 methylaniline, 424

 OCTAMETHYLENE, 450
 Oleic acid, 169
 Optical rotation, 119, 245, 251
 Orientation, 309
 Osazones, 273, 379
 Oxalic acid, 161, 163, **184**
 Oxamic acid, **183**
 Oxamide, 187
 Oxanthranol, 421
 Oxidation, 29
 Oximes, **144**, 268, 385
 Ozokerite, 75
 Ozonides, 83

 PALMITIC ACID, 166
 Paracyanogen, 222
 Paraffins, 73.
 Paraldehyde, 149
 Pararosanine, 433
 Pararosolic acid, 437
 Pentachloroethane, 11
 Pentamethylene, 450
 Pentoses, 271
 Perkin, 433
 reaction, 396
 Petroleum, 74

 Phenanthrene, 409
 Phenetole, 343
 Phenol, **341**, **318**, 334, 337, **341**, **373**,
 426, 427
 phthalein, 398, 439
 sulphonic acids, 341, 426
 Phenoxides, 338
 Phenyl ether, 343
 salicylate, 401
 sulphide, 375
 Phenyl-acetic acid, 396
 acetonitrile, 396
 alanine, 295
 aminosulphonic acid, 424
 carbonic acid, 427
 Phenylenediamine, **364**, 382, 383,
 426, 430
 Phenyl-glucosazone, 380
 glyceric acid, 397
 glycollic acid, 403
 hydrazine, 377, **378**, 383, 426
 hydrazones, 144, 379, 385
 hydroxylamine, **356**, 381, 426
 methylcarbinol, 389
 methylnitrosoamine, 424
 nitromethane, 352
 propionic acid, 397
 sulphuric acid, 426
 Phloroglucinol, 348
 Phorone, 154
 Phosphine oxides, 239
 Phosphines, 238
 Phosphinic acids, 239
 Phosphonium salts, 238
 Phthalamide, 398
 Phthalanil, 399
 Phthaleins, 439
 Phthalic acids, 322, **397** —
 anhydride, **398**, 420
 Phthalide, 398
 Phthalimide, 398
 Phthalyl chloride, **398**, 420
 Picolines, 456
 Picolinic acid, 456
 Picramide, 355, **371**
 Picric acid, **354**, 432
 Picryl chloride, 354, 372
 Pimelic acid, 318
 Pinacoline, 156
 Pinacone, 152, 156
 Pinene, 454
 Piperazine, 205

Piperidine, 455
 Polyoxymethylene, 147
 Polypeptides, 293
 Primary alcohols, 106, 108
 amines, 200

Proline, 294
 Propane, 11, 79
 Propargyl alcohol, 127
 Propionic acid, 165
 Propionitrile, 221
 Propyl alcohol, 116
 Propylene, 16, 85
 bromide, 104
 glycol, 130

Proteins, 293
 Purin, 298
 Purpurin, 445
 Purpuroxanthin, 445
 Pyridine, 455
 Pyrogallol, 348
 Pyrrole, 458
 Pyrrolidine, 458
 Pyruvic acid, 258

QUATERNARY ammonium salts, 200,
 202
 phosphonium salts, 238
 iol (*see* HYDROQUINONE).
 oline, 456
 one, 346, 362, 426
 onoid compounds, 346, 347,
 37, 419, 429, 434, 440, 442

EMIC acid, 251
 emission, 253
 inose, 283
 uction, 29, 111, 304, 451
 er's reaction, 387, 427
 lution, 252
 rcinol, 344
 aniline, 436, 438
 olic acid, 439
 erythric acid, 444

CHARIC acid, 275
 charin, 404
 charose (*see* CANE-SUGAR).
 cin, 389
 icylaldehyde, 387

Salicylic acid, 318, 400, 427
 Saligenin, 389
 Sandmeyer reaction, 328, 375
 Sarcosolactic acid, 244
 Schiff's reagent, 275, 278
 Schotten-Baumann reaction, 393
 Secondary alcohols, 106, 109
 amines, 201

Silicanes, 232
 Skraup's quinoline synthesis, 457
 Soaps, 130, 166
 Sorbitol, 134, 275
 Starch, 283
 Stearic acid, 166
 Stibines, 240
 Succinamide, 191
 Succinic acid, 189
 anhydride, 190
 Succinimide, 191, 297, 458
 Sucrose (*see* CANE-SUGAR).
 Sulphanilic acid, 362, 369, 424
 Sulphides, 23, 211, 336
 Sulphinic acids, 214, 335
 Sulphobenzoic acids, 401, 403
 Sulphochlorides, 215, 333
 Sulphonol, 214
 Sulphonamides, 215, 334
 Sulphonation, 321, 332, 429
 Sulphones, 213, 336
 Sulphonie acids, 214, 332
 chlorides, 215, 333
 esters, 215, 333
 Sulphonium salts, 213
 Sulphoxides, 213, 336

TARTARIC acids, 249
 Tartronic acid, 133
 Tautomerism, 225, 261, 297, 349
 Terephthalic acid, 323, 324, 399
 Terpenes, 324, 455
 Tertiary alcohols, 107, 109
 amines, 202
 Tetrachloroethane, 11
 Tetrahydro-naphthalene, 411
 naphthols, 415
 naphthylamines, 416
 Tetramethyldiamino-benzophenone,
 367
 diphenylmethane, 367
 Tetramethylene, 450
 Tetranitromethane, 208

tetraphenylmethane, 325
 Theobromin, 298
 Thioacetic acid, 211
 Thiocarbamide, 183
 Thiocyanates, 183, 226
 Thiophene, 459
 Thiophenols, 335, 375
 Thiourea (*see* THIOCARBAMIDE).
 Thymol, 342, 453
 Tin alkyls, 233
 Toluene, 305, 321
 Toluic acids, 395
 Toluidines, 363, 425
 Triaminotriphenylmethane, 434, 435
 Tribromo-aniline, 361
 hydrin, 100
 phenol, 340
 Trichloro-acetic acid, 152
 acetyl chloride, 160
 benzene, 422
 ethane, 10
 Trimesic acid, 324
 Trimethylamine, 204
 Trimethylene, 450
 bromide, 104, 450, 456
 glycol, 130
 Trinitro-aniline, 371
 anisole, 355, 372
 benzene, 351
 phenol, 354, 432
 toluene, 321
 triphenylmethane, 433
 Trioxymethylene, 147
 triphenyl-amine, 368
 carbinol, 325
 methane, 325, 433
 methane dyes, 432
 Tyrosine, 295, 405
 URANIN, 441
 Urea (*see* CARBAMIDE)
 Urethanes, 181
 Uric acid, 296
 VALINE, 291
 Vanillin, 387
 Vapour-density, 64
 Vinyl alcohol, 149
 halides, 100
 WÖHLER, 180
 Wurtz reaction, 77, 321
 XANTHATES, 183
 Xanthin, 298
 Xylenes, 308, 322
 Xylidine, 425
 Xylitol, 134
 Xylose, 271
 YEAST, 114
 ZINC alkyls, 233
 Zymase, 114, 281

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